

IMPROVED SEPARATORS FOR SILVER OXIDE-ZINC  
AND SILVER OXIDE-CADMIUM CELLS  
FOR SPACECRAFT APPLICATION

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FIGURE

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### PROJECT PERSONNEL

In carrying out the experimental work herein reported, the writers were assisted at The Borden Chemical Company by Dr. Kitazawa, Head of the Physical Testing Laboratory, Mr. Richard Trickey, chemist, and Messrs. Ronald G. Burton, Charles J. Guinosso and Charles Kelly, assistants. At Burgess Battery Company, the subcontract tests were supervised by Mr. Frederick A. Poss.

## INTRODUCTION

This report summarizes the progress made under Contract NAS-5-9107 during the period November 10, 1964 to November 10, 1965. Sections A through D cover in detail the experiments carried out during the fourth quarter of that period.

The chief aims of the studies herein described were to improve upon the properties of the membranes developed under the previous contract NAS-5-3467. Extensive life-cycle tests (5) of certain of these membranes in secondary silver zinc cells at the Naval Ammunition Depot at Crane, Indiana, have shown that modifications of methyl cellulose, exemplified by types C3 and B3, extended cell-life fivefold and, in particular, prevented catastrophic shorting due to zinc dendritic growth. The continued work covered in this report took three approaches:

- 1) The types of membranes developed in the preceding Contract were studied in greater detail with particular emphasis on their permeability to and reaction with silver ions.

- 2) Further modifications of methyl cellulose formulation were aimed at increased conductivity of electrolyte-swollen films - particularly desirable when the swelling electrolyte is potassium hydroxide in concentrations greater than 30%.

- 3) Synthesis of new polymers was undertaken to explore the possibility of combining within the same molecule the balance of polarity needed for efficient separator performance.

## SUMMARY AND CONCLUSIONS

1) Diffusion of silver through representative membrane types was studied with radioactively tagged silver oxide in 30% KOH. The technique was improved to account more accurately for original, diffused and separator-reduced silver.

2) Silver diffusion through methyl cellulose-polyacid films occurred at rates which were higher when the polyacid proportion was higher. Degree of swelling in electrolyte also increased with polyacid proportion. Films of this category are resistant to oxidative attack and physical degradation. Examples have resisted catastrophic termination in cell tests.

3) Cellophane, polyvinyl alcohol, hydroxypolyvinyl alcohol (HEPVA) and hydroxyethyl cellulose-methyl cellulose films held back silver virtually completely, but were extensively oxidized and physically degraded in the process. The high reducing power of these membranes is associated with their abundance of readily oxidizable hydroxyl groups. In cell tests, they have in common the tendency toward eventual short circuit.

4) Films in which methyl cellulose is the sole polymer were improved about twenty-fold in conductivity in 45% KOH by depositing them from a solution containing six parts potassium hydroxide per hundred of methyl cellulose. Similar applications of sodium, lithium and barium hydroxides were studied over a range of proportions. A film of this type (#12) was tested in cells at Burgess and was still in operation after 37 cycles at termination of contract.

5) Improvement in conductivity (up to 100-fold) of methyl cellulose was achieved also by depositing film from solutions containing salts of various organic acids (10 to 30% of polymers). The salts were extractable by excess electrolyte. Films of this type possess improved flexibility even at low humidities, a property attributable to hygroscopicity of the salts. Fifteen cells have been prepared by Burgess using Film #15, which is a 9:1 formulation of methyl cellulose and PVM/MA plus 28% on polymer of potassium lactate.

6) Conductivity of methyl cellulose films in 45% KOH was improved about 100-fold by preswelling in 15% KOH. After exposure of the pre-swollen film to stirred 45% KOH for seven days, the over-all weight pick-up was 61% in contrast to only 22% when methyl cellulose was equilibrated directly in 45% KOH.

7) Conductivity of methyl cellulose-polyacid formulations in 45% KOH was improved up to 100-fold by depositing the films from solutions containing 10%, on weight of polymer, of low molecular weight amines. The amines were extractable by excess electrolyte. Although two out of three films (#10, #11, #13) representing this type in cell tests at Burgess terminated by short circuit, further tests are considered justified.

8) Coacervation of methyl cellulose and polyacids with polyethyl-enimine led to films with decreased conductivity, as would be expected from tightly entangled polymers crosslinked by Coulombic bonds.

9) Methyl cellulose was chemically modified by replacing the hydrogen of the residual hydroxyl groups with carboxy methyl. Conductivity was improved about 20-fold over the C3 type (7:3 methyl cellulose/PVMMMA). This synthesis was not developed because cumbersome purification steps appeared to make it impractical.

10) Several water-soluble derivatives of cellulose were investigated. One of these, a commercial grade of hydroxyethyl ethyl cellulose had conductivity similar to methyl cellulose. Burgess tests in cells of a formulation with PVMMMA (#8) were inconclusive.

11) Addition copolymers containing various proportions of polar and non-polar groups were synthesized. Although polymers were produced which gave conductivities in the useful range when supported on Dynel cloth, none of them combined the required properties of strength, flexibility and conductivity for preparing unsupported membrane.

12) Modified polyethylene polymers containing phosphonic acid groups were synthesized. Work was discontinued in this area because of problems in scaling up.

13) A copolymer of ethylene and acrylic acid gave conductivity in the useful range but this film was too weak and brittle as an unsupported membrane.

14) In cell tests at Burgess, two variants of C3 film representing improvements in purification and film preparation did not show corresponding improvements in performance.

15) In cell tests at Burgess, a laminate of C3/PVAlc/C3 (Film #5) showed a good capacity in early life and had run 66 cycles when terminated because of low output. Because this film also promises to be of value in holding back silver during charged stand, it has been chosen for further testing by NASA.

16) The fifty cells required by contract were constructed at Burgess with the following experimental films:

<u>Film Number</u>	<u>Description</u>	<u>cf. item in this summary</u>
#5	C3/PVAlc/C3 laminate	15
#8	Ethulose/PVMMMA	10
#12	Methyl cellulose, 6% KOH	4
#14	Methyl cellulose, 9% KOH	4
#15	C1 plus 28% K lactate	5



#### A. Modification of Methyl Cellulose/Polyacid Films with Amines

In the Third Quarterly Report under the current contract (pp 2-10), it was shown that the addition of amines to methyl cellulose/polyacid formulations lowers electrolytic resistance. This effect was of sufficient magnitude to permit reduction of the polyacid content with consequent improvement in flexibility of the resulting film.

It is reasonable to conjecture that the acid-base equilibrium of amine with both carboxyl and hydroxyl groups of the macromolecules competes with the tendency of the macromolecules to hydrogen-bond with each other, thus decreasing the tortuosity of the electrolyte-imbibing paths within the film. This alone would be expected to increase conductivity. The question arises to what extent the subsequent extraction of the amine by supernatant electrolyte plays a part in increasing conductivity.

The extractability of amines by excess supernatant electrolyte is illustrated by the data in Table I, which shows that after seven days exposure to unstirred 45% KOH solution only about 2% of the original amine in C2A film remained unextracted by the electrolyte. On exposure for a similar period to a large excess of 30% KOH, all the amine was extracted. Corresponding experiments on films containing either triethanolamine or methoxy propylamine as the modifying amine also showed complete removal of amine by excess electrolyte.

Table I

Extraction By Potassium Hydroxide Solutions of 3-Hydroxypropylamine (a)  
from C2A Film (b)

Sample	Days Exposure to KOH Solution	Concentration of KOH Solution	Agitation Conditions	Weight Ratio Solution to Film	Percent Nitrogen		
					in film Calcd. (c)	Recovered in Electrolyte (d)	Found
0	0	-	-	-	2.12	1.83	-
1	7	30	rapid	435	-	0.00	1.90
2	7	30	rapid	435	-	0.00	-
3	7	45	stagnant	10.4	-	0.04	-

- (a) Source of hydroxypropylamine was American Cyanamid Co. Purity by titration, 95%; Nitrogen content by calculation was 18.64%, by direct Kjeldahl analysis 18.25%.
- (b) Composition of C2A film is methyl cellulose 80 parts by weight, poly(vinylmethyl ether-maleic anhydride) 20 parts, hydroxypropylamine 10 parts. Preparation 499-7E.
- (c) Calculated nitrogen based on film composition (see b) and data in (a).
- (d) Amine recovered from supernatant electrolyte by steam distillation and titration.

The experiments summarized in Table II were made on B2A' film containing methoxypropylamine which is less soluble in concentrated C2A' solutions than hydroxypropylamine and which would therefore be expected to be less extractable by electrolyte. Weight pick-up and residual amine content by Kjeldahl method were measured on film samples which were steeped in a shallow layer of 45% KOH in covered Petri dishes. The weight ratio of electrolyte solution to original film was approximately 10. Samples were removed periodically from their respective dishes and blotted with filter paper before weighing and analysis. The results of Table IIa show that the film reached its maximum swollen weight and minimum amine content after 40 minutes exposure to electrolyte. At this point it had lost more than half its original amine. Beyond this point in time, the weight of swollen film and, within experimental error, the amine content remained unchanged. Table IIb shows the change in resistivity with time of a single piece of C2A' film from the time it was inserted dry into a conductivity cell. Since the ratio of electrolyte to exposed film is much greater than in the case of the Petri dish experiment, it might be expected that properties would continue to change over a longer period of time before equilibration. This is indeed the case; resistivity continues decreasing beyond 40 minutes and decreases approximately tenfold further before reaching a steady value. Since the amine content of the film in the conductivity cell is not known, it is uncertain to what degree the lower resistivity is related to further removal of amine. Another factor deserving consideration is the gradual decrease of tortuosity of conducting paths as the swollen film equilibrates with the imbibed electrolyte. Also, the effect of electric field on the opening of electrolytic paths has not been studied.

Table II

Effect of Continued Exposure to 45% KOH on Properties of C2A' Film  
(10 parts C2 plus 1 part Methoxypropylamine) Ref. 522-111

a) Swelling and Amine Loss			b) Electrolytic Resistance	
Time	Ratio of Swollen Wt./Orig. Wt.	% Amine in Film by Kjeldahl Nitrogen Analysis	Time	Resistivity Milliohms.-in. <sup>2</sup>
0	1.00	9.15	3 min.	$1.35 \times 10^6$
5 min.	1.21	-	5 "	$7.9 \times 10^5$
10 "	1.37	4.85	10 "	$1.5 \times 10^5$
20 "	1.46	-	15 "	$1.3 \times 10^4$
40 "	1.54	4.05	20 "	566
60 "	1.56	4.40	40 "	308
2 hrs.	1.57	-	60 "	217
4 "	1.56	-	24 hrs.	25
24 "	1.56	-	72 "	44
72 "	1.54	-		

In view of the results obtained with amines of low molecular weight, interest was renewed in the applications of the polymeric amine, polyethylenimine. Earlier experiments with this amine under the previous Contract illustrated its difficulty in forming uniform continuous films with polymers containing carboxy and or hydroxy groups. Even in the preparation of solution mixtures there is a tendency to coacervate with the precipitation of water-insoluble curds from which films cannot be easily prepared. It has since been found that polyethylenimine is compatible with a polyacid solution which has first been neutralized with ammonia. Clear homogeneous solutions can be formed containing both polyethylenimine and polyacrylic acid, for example, both with and without methyl cellulose. Thus a B2 solution, after addition of sufficient ammonia to bring pH to 9.3, will accept up to 20% of polyethylenimine on weight of B2 polymer without clouding. The data of Table III were obtained on films cast from such ammoniacal solutions. Ammonia as well as water was evaporated in formation of these films. It is evident that resistivity of these films becomes greater as the polyethylenimine content is increased. This is attributable to tightly entangled polymers crosslinked at many loci by the Coulombic bonds of salt formation. Such structure prevents imbibition of KOH sufficient to provide easy conducting paths through the membrane phase. Because several such Coulombic bonds are effective along each entangled chain, even though each of these may be momentarily broken by the combined effect of heat motion and kinetic interchange of protons, there is very little chance for all the bonds on a chain to be broken simultaneously and permit migration of the polymeric amine into the aqueous phase. It is therefore to be expected that such films could not be made more conductive by even prolonged exposure to excess KOH solution.

Table III

Properties of Polyethylenimine Modified B2 Films (a) (10% solids B2 solution first brought to pH 9.3 with aqueous ammonia)				
Exp't. Reference	PEI (b) parts added to 100 parts B2 (a)	Electrolytic Resistivity in 45% KOH milliohms-in. <sup>2</sup>	MIT Flex at 200 g tension	
			Film thickness mils	Cycles
522-8	0	207	-	-
522-9	3	422	1.5	2908
522-10	6	1960	1.6	2002
522-11	10	4000	2.3	(65)
522-12	20	5570	1.6	1197

(a) B2 is 20% by weight polyacrylic acid Acrysol A5 (Rohm & Haas), 80% methyl cellulose (Dc: Methocel 15).

(b) PEI is polyethylenimine, Monomer-Polymer Division, Borden Chemical Co.

## B. Modification of Methyl Cellulose with Hydroxide Bases

Experiments on the carboxymethylation of the residual hydroxy group of methyl cellulose were described in the Second Quarterly Report (6) of the current Contract (pages 7 and 8). It was found that the purified reaction product still contained traces of sodium hydroxide, sodium chloroacetate, sodium chloride and sodium glycolate. It was therefore pertinent to investigate the effects of these substances on film resistivity. Unexpectedly large effects were found not only on the carboxymethylated product but also on methyl cellulose itself. This led to a more systematic investigation of the addition of bases and salts to methyl cellulose. The effect of amines has been discussed in the preceding Section A. Compositions with salts of organic acids are described in the following Section D. The present Section covers hydroxide bases with inorganic cations or quaternary ammonium ions.

It is evident from the data in Table IV that sodium and potassium hydroxide had the greatest effect among the inorganic bases in lowering the electrolytic resistance of methyl cellulose. This effect may be expected to be dependent also on the compatibility of the base with the polymer. Lithium hydroxide frosted out from the film in well defined crystals, indicating that very little was soluble in the film itself. Barium hydroxide was also extensively frosted out. Both bases are of limited solubility in water as compared to sodium and potassium hydroxide and the latter appeared to be more compatible with the methyl cellulose.

In the last line of Table IV the properties of a typical C3 film are given for comparison. The C3 formulation contains no base and is prepared from 3 parts poly(vinyl methyl ether/maleic anhydride) with 7 parts methyl cellulose. In the case of alkali metal hydroxides, the swollen weight to dry weight ratio showed a 30 to 40% pick-up as against a 70% pick-up in the case of C3, while giving a comparable or even lower resistance. In interpreting these facts, it must be remembered that the overall imbibition of electrolyte is not the only factor contributing to conductivity. The tortuosity of the path through which electrolytic migration takes place also is an important parameter. The presence of amines or hydroxides during deposition of the film tends to lower the hydrogen bonding of methyl cellulose molecules with each other, tending to create a more open structure.

Table IV

Methyl Cellulose Plus Bases

Refer- ence		Base -	Elec.	Swollen Wt./	MIT Flex	200 g Ten-		Ten- sile psi	Notes
		% on . Methyl Cellu- lose	Resist. in 45% KOH milli- ohms-in. <sup>2</sup>	Dry Wt. 30% KOH	Wt. 45% in KOH	sion (A)	mils cycles		
421-86	none	0	7250	1.23	1.25	1.4	5355		
522-1	LiOH	3	3030	-	-	1.5	3341	8100	F
522-2	LiOH	6	4660	-	-	1.5	1399	4320	F
522-3	LiOH	10	2180	-	-	1.5	827	3100	F
522-4	LiOH	20	2340	-	-	1.5	855	2240	F
504-132	NaOH	3	1655	1.36		1.4	2853	11100	SF
504-133	NaOH	6	330	1.32	1.34	1.6	2233	8500	SF
504-134	NaOH	10	0	1.44	1.37	1.5	654	7890	SF
482-49	KOH	3	1320			1.3	5118	8030	-
482-54	KOH	6	330	1.34	1.28	1.4	3100	8870	
482-55	KOH	9	154			1.5	2272	7350	DF
482-50	KOH	15	31			1.5	506	-	F
504-56	Ba(OH) <sub>2</sub>	9	18920	-	-	-	-	-	F
504-139	Bz(Me) <sub>3</sub> NOH	10	1520	-	-	1.5	4745	-	SF
504-140	Bz(Me) <sub>3</sub> NOH	5	7260	-	-	1.6	4024	-	SF
482-60	HOCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	14	573	-	-	1.7	3216	8140	
482-99-1*	482-54 + CO <sub>2</sub>	6	400	-	-	-	-	-	-
482-99-2*	504-133 + CO <sub>2</sub>	6	437	-	-	-	-	-	-
485-89	C3	none	387	1.72	1.69	1.5	754	14700	

Notes to Table IV -

- F = Frost out of the added base as crystals.  
 SF = Slight frost out, milky. Colloidal?  
 DF = Delayed frost out. Clear film turned milky on standing  
 (A) ASTM  
 \* Exposed to current of carbon dioxide for 24 hours.

This view is supported by the results summarized in Table V, of experiments which studied the change in potassium content of KOH-modified films on exposure to 30% KOH solution. A weighed accordion-pleated film was placed in a quart jar with a large excess of 30% KOH and a magnetic stirrer enclosed in a small beaker to prevent direct contact between the film and stirrer. The jar was covered and allowed to stand with continuous stirring for periods of 12 or 32 days respectively. Ash analysis was then carried out on weighed blotted film. Corresponding ash analyses were also made on original film. Unmodified methyl cellulose films were studied in parallel with KOH-modified films. Total KOH content of the equilibrated film (calculated from ash content) of the KOH-modified films corresponded fairly closely to the KOH originally dispersed in the film plus imbibed 30% KOH corrected for displacement of original moisture. It is therefore likely that the presence of KOH within the film during its formation contributes to additional paths of conductance.

Permeability of KOH-modified films to silver ion is under investigation, using radioactive tracer techniques.

Table V

Intensive Stirring of KOH-Impregnated Methyl Cellulose Films  
in 30% KOH

Expt. No. Composition	483-129		504-150	
	Methyl Cellulose + 6% KOH	Methyl Cellulose (Control)	Methyl Cellulose + 6% KOH	Methyl Cellulose (Control)
Days stirred	32	32	12	12
% MC uncorr.	99.34	100.0	94.34	100.0
% KOH uncorr.	5.66	-	5.66	-
% Moisture in film	9.0	9.3	9.0	9.3
(D) % MC corr. for moisture	85.85	90.7	85.85	90.7
(E) % KOH corr. for moisture	5.15	-	5.15	-
(F) % Moisture	9.0	9.3	9.0	9.3
(A) Wt. film 50% R.H. g	.3242	.3290	1.2867	1.5801
(B) Wt. film after stirring in 30% KOH g	.4358	.4047	1.6732	1.9321
(C) Wt. increase in 30% KOH	.1108	.0757	.3865	.3520
% increase wt.	34	23	30	22
Sulfate ash on blotted film g	.0888	.0515	.3079	.2262
(G) KOH equiv. ash g	.0572	.0331	.1980	.1455
(G/B) KOH in blotted film %	<u>13.10</u>	<u>8.20</u>	<u>11.83</u>	<u>7.52</u>
Calculated KOH in Blotted Film				
(A x E) Orig. KOH added g	.0167	-	.0652	-
(C x .30) KOH absorbed g	.0332	.0227	.1159	.1055
(A x F x .30) KOH replacing moisture g	.0087	.0092	.0347	.0440
(H) Total Calcd. KOH g	.0586	.0319	.2158	.1485
(H/A) Calcd. KOH in blotted film %	<u>13.40</u>	<u>7.90</u>	<u>12.80</u>	<u>7.70</u>

### C. Modification of Methyl Cellulose by Preswelling

Methyl cellulose is considerably more swollen at lower KOH concentrations than conventionally used as electrolyte. A methyl cellulose film was swollen by equilibrating in 15% KOH, the degree of swelling noted, the film then vigorously stirred in 45% KOH for seven days, after which the degree of swelling was again determined and the electrolytic resistance measured at that concentration. As shown in Tables VIa and VIb the swelling imparted at the lower concentration was substantially retained at 45%. The electrolytic resistance was low, 60 milliohms.-in.<sup>2</sup> or about the order of cellophane (around 30). Ash analysis on the blotted film showed a high value for KOH, indicating the lowered resistance was due to large voids in the film, now replaced by 45% KOH. It will be pertinent to determine the permeability of such a film to silver and zinc ion as well as KOH.

Table VIa

Effect of Preswelling A Methyl Cellulose Film in 15% KOH  
on Its Electrolytic Resistance in 45% KOH

		Preswollen in 15% KOH	Directly In 45% KOH
Swollen Wt./Orig. Wt.	15% KOH	1.68	-
Swollen Wt./Orig. Wt.	45% KOH	1.61*	1.22
Resistance in 45% KOH - milliohms-in. <sup>2</sup>		60	6080

\*Film soaked 3 days in 15% KOH, blotted, then stirred 7 days in large excess 45% KOH. See Table VIb.



Table VIb

KOH Content of Above Films by Ash Analysis

		Preswollen in 15% KOH	Directly in 45% KOH
% MC at 50% R.H.		90.7	90.7
% H <sub>2</sub> O		9.3	9.3
(A) Wt. Film at 50% R.H.	g.	.6518	1.5801
(B) Wt. Film 3 days in 15% KOH	g.	1.0958	-
(B') Wt. Film B after 7 days stir in 45% KOH	g.	1.0498	1.9321
(B)/(A)		1.685	
(B')/(A)		1.612	1.22
(C) KOH equiv. ash in film from 45% KOH	g.	.2110	.2296
(C)/(B') KOH in film from 45% KOH	%	<u>20.1</u>	<u>11.9</u>
Calcd. KOH in film from 45% KOH			
KOH absorbed (B'-A) x .45		.1790	.1583
KOH equiv. orig. moisture A x .093 x .45		.0272	.0660
(D) KOH total		.2062	.2243
Calcd. % KOH (D)/(B')		<u>19.65</u>	<u>11.6</u>

#### D. Modification of Methyl Cellulose with Salts of Organic Acids

Pursuing the incidental finding that sodium glycolate lowered the resistance of methyl cellulose, the lithium and potassium salts of formic, acetic, propionic, butyric, salicylic and lactic acids were studied as additives. The salts exhibited a remarkable degree of compatibility with the methyl cellulose. Although lithium formate and lithium salicylate, which were the least soluble, showed some frosting, it was not as great as with lithium hydroxide and the increase in conductivity is greater with lithium salts than with lithium hydroxide. Results, summarized in Tables VII and VIII, show that the resistance tends to be related to the molar proportion of the salt added. It is interesting that on a weight basis this class of additives is more efficient than the polyacids in lowering the resistance of methyl cellulose.

The degree of solubility from the films into the electrolyte was determined by exhaustive stirring, followed by ashing the blotted film as described under the preceding section. Preparation 534-58 of Table VII (33% K propionate) and preparation 482-121 (28.6 K butyrate) each gave ash values which corresponded to total replacement of the original salts with electrolyte. Preparation 522-49 (28% potassium lactate) and preparation 534-8 (32.7 K acetate) gave ash values which were in ranges corresponding to partial retention of the salts by the films after the stirring.

Table VII.

## Modification of Methyl Cellulose Films with Salts of Organic Acids

Ref- erence	Additive	Amount Added to MC			Notes	Elec. Res. 45% KOH milli- ohms-in <sup>2</sup>	50% R.H. Properties			
		As acid	As salt	moles per equiv MC*			MIT Flex		Tensile	
		%	%				mils	cycles	psi	Elong. F
522-68	Li Formate	3	3.4	.122		2045	1.6	3599	9660	40
-69	(M.Wt. 52)	6	6.8	.244	F	616	1.6	4306	8440	44
-70	"	10	11.3	.408	F	151	1.5	3900	6790	56
-71	"	20	22.6	.82	F	88	1.9	2535	6640	40
522-72	K formate	3	5.5	.122		1810	1.5	4048	8800	35
-73	(M.Wt. 84)	6	10.9	.244		395	1.5	3286	6600	30
-74	"	10	18.2	.407		160	1.7	3141	6020	38
-75	"	20	36.4	.814	E,C	79	1.8	2705(c)	3858	39
534-6	K Acetate	6	9.8	.19		399	1.6	5130	8320	48
-7	(M.Wt. 98)	10	16.3	.313		137	1.8	6152	6490	54
-8	"	20	32.7	.624		34	2.0	5188	3570	48
534-56	K Propionate	6	9.1	.153		515	1.5	5234	8040	47
-57	(M.Wt. 112)	10	15.1	.254		147	1.8	5015	6290	51
-58	"	20	30.3	.506		50	1.9	12230	3540	57
534-91	K Butyrate	10	14.3	.213		226	1.4	5154	-	-
482-121	(M.Wt. 126)	20	28.6	.427		110	1.4	7591	-	-

Table VIII

## Modification of Methyl Cellulose Films With Salts of Organic Acids

Ref- erence	Additive	Amount Added to MC			Notes	Elec.Res. 45% KOH milli- ohms-in. <sup>2</sup>	50% R.H. Physical Properties		
		As acid %	As salt %	moles per equiv. MC(*)			MIT Flex		Tensile
							mils	cycles	psi Elong. %
522-38	Li Lactate	2.62	2.8	.054		2700	1.3	4677	9850 23
-39	(M.Wt. 96)	5.23	5.6	.109		1345	1.6	3672	10260 33
-40	"	8.74	9.3	.182		886	1.5	5642	7858 28
-41	"	17.5	18.7	.364	%	144	1.5	7456	6810 40
522-46	K Lactate	3.0	4.26	.062		2225	1.4	5024	9611 23
-47	(M.Wt. 128)	6.0	8.50	.124		875	1.5	4172	9060 42
-48	"	10.0	14.2	.208		295	1.4	5672	7800 43
-49	"	20.0	28.4	.416	(C)	170	1.6	8449(C)	5840 43
522-42	Li Salicylate	3.0	3.1	.041		5220	1.5	4199	10100 16
-43	(M.Wt. 144)	6.0	6.3	.083		2980	1.5	3022	9430 19
-44	"	10.0	10.4	.136		1600	1.5	2536	8940 11
-45	"	20.0	20.9	.291	P,B	650	1.5	1598	8090 12
522-50	K Salicylate	3.0	3.8	.041		3170	1.3	4128	9390 15
-51	(M.Wt. 176)	6.0	7.7	.082		1840	1.4	3388	8750 11
-52	"	10.0	12.7	.135		692	1.4	2978	9290 15
-53	"	20.0	25.5	.270	P,B	339	1.4(B)	1206	8660 9

## Notes to Table VIII

\* Methyl cellulose at 1.8 degree of substitution per anhydroglucose unit  
= ca. 188

F = The additive frosted out of the air-dry film.

E = Barely perceptible liquid exudate at 50% R.H.

P = Erratic flex values, and appearance suggested localized insoluble particles.

B = Extremely brittle at 18% R.H., cracking when handled.

C = Quite flexible at 18% R.H. See Table IX.

It was observed that several of the film compositions were not only more flexible than methyl cellulose itself at 50% R.H., but remained flexible under low humidity conditions. Representative films were compared in the flex test at 50% and 18% relative humidity, as shown in Table IX.

Table IX

Methyl Cellulose-Organic Salt Films - Flexibility-Relative Humidity Relationship

Reference	Composition	Thick- ness mils	MIT Flex 72° F.		Elec. Res. 45% KOH Milliohms- in. <sup>2</sup>
			14% R.H. cycles	50% R.H. cycles	
522-49	MC 15 + 28.4% K lactate	1.6	4447	8449	170
522-95	Cl + 28.4% K lactate	1.5	898	8851	98
522-75	MC 15 + 36.5 K formate	1.8	1827	2705	79
522-40	MC 15 + 9.3 Li lactate	1.5	2410	7858	886
522- 5	MC 15 + 20.9% Li salicylate	1.5	1	1598	650
522-53	MC 15 + 25.5% K salicylate	1.4	106	1206	339
MP 146-49 C3		1.5	30	627	378
522-98	B2 + 10% 3-methoxy- propylamine	1.5	255	8000	44
502-26	C2 + " "	1.5	106	3789	47

It is evident that with the exception of the salicylates the salts showed much greater retention of flexibility at low humidity levels than other representative formulations. This is related to the hygroscopicity of the salts.

#### E. Silver Diffusion Studies, Using Radioactively Tagged Silver Oxide

As reported in detail in the First Quarterly Report, Section A, a study was made of the diffusion of silver ions from saturated solutions of silver oxide in 30% KOH through various membranes equilibrated with these solutions. The radioactive tracer procedure employed an apparatus based on Dirkse (1) and Weiss et al. (2) but incorporating improvements which avoid silver losses on the walls of the cell. The half-cells are standard commercial pyrex cells with one-inch internal diameter. These are clamped with aluminum flanges using polyethylene gaskets on both sides of the membranes to be tested. Circular disks, 1.5 inches in diameter, were cut by a punch. Stirring was magnetic with half-inch Teflon bars. Neoprene stoppers on each half-cell were not allowed to contact the silver solution and were fitted with capillary tubes to equalize pressure.

The radioactive solution was prepared by treating 30% KOH with  $\text{AgNO}_3$  solution enriched with  $\text{Ag}^{110}$ . The amount of  $\text{AgNO}_3$  was just in excess of that necessary to saturate the solution with silver oxide.

In each experiment, the clean dry cell was assembled with membrane (conditioned in the electrolyte) inserted between the two sides. A 45.0 ml portion of radioactive stock solution was then pipetted into Side 1. Immediately thereafter, a 45.0 ml portion of a corresponding non-radioactive silver was pipetted into Side 2. Periodically, duplicate 0.05 ml aliquots were pipetted from each side to stainless steel planchets. After infra-red drying, radioactivity was measured with a scaler and flow-counter. Counts were corrected for noise count.

Typically, the observed counts per minute changed from more than 400 to about 200 on the initially radioactive Side 1. Noise count was usually about 30. Statistical analysis of a large number of duplicate 0.05 ml samples showed standard deviation of  $\pm 10$  counts, corresponding to standard error from 2.5 to 5.0% on Side 1 as radioactivity decreased.

Table X summarizes data at conclusion of experiments, including concentrations of radioactive silver oxide respectively remaining on initially radioactive Side 1, and diffused to Side 2, together with corresponding amounts taken up by membrane. The latter was also corrected by factor of 2 to convert to total taken from both sides. In converting count into silver oxide weight, 57 mg per liter was used as the solubility in 30% KOH at 25° C. (3).

Deviation of radioactive "sum" from 2.57 is a measure of precision.

Table X

Silver Diffusion at 25° C. Through Membranes from 30% KOH Solutions  
Saturated with Ag<sub>2</sub>O

Membrane	Time (hours)	Disposition at End of Experiment of 2.57 mgs. Ag <sub>2</sub> O originally on side 1. - in milligrams (Estimated from Radio- activity)				Total Ag <sub>2</sub> O Taken Up By Membranes From Both Sides (in mg.)
		Side 1	Side 2	Membrane	Sum	
(1)	146	0.62	0.11	1.76	2.49	3.54
(2)	66	.89	.06	1.88	2.83	3.76
(3)	92	1.08	.07	1.81	2.96	3.62
(4)	66	.72	.08	1.76	2.56	3.51
(5)	66	2.04	.39	0.03	2.46	0.065
	146	1.49	1.03	.10	2.62	.195
	188	1.65	1.21	.13	2.99	.265
(6)	118	2.16	0.37	.23	2.76	.449
(7)	173	1.56	.80	.17	2.53	.346
(8)	66	1.71	.39	.14	2.24	.279
	161	1.41	.85	.33	2.59	.665
	188	1.43	1.14	.23	2.80	.467
(9)	92	2.03	0.11	.08	2.22	.158
	173	1.84	.61	.04	2.49	.079

Membranes in Table X are identified as (1) Cellophane PUDO;  
(2) 8 parts 88% hydrolyzed PVALc., 2 parts tetraethylene glycol;  
(3) completely hydrolyzed PVALc; (4) 6.5 parts methyl cellulose,  
3.5 parts hydroxyethyl cellulose (HEC); (5) 7 parts methyl cellulose, 3 parts  
polyacrylic acid (B3); (6) 9 parts methyl cellulose, 1 part PVMMA (1:1  
copolymer of vinyl methyl ether and maleic anhydride) (C1); (7) 8 parts  
methyl cellulose 2 parts PVMMA (C2); (8) 7 parts methyl cellulose 3 parts  
PVMMA (C3); (9) Copolymer S, a proprietary product derived from a synthetic  
latex.

Three types of behavior are illustrated in Table X.

(1) Membranes with cellophane, PVALc or HEC reduce silver oxide to metallic silver. During the course of a diffusion experiment the loss of radioactivity on Side 1 is at first more rapid than the gain on Side 2, indicating that passage through the membrane is initially halted. However, these membranes are eventually damaged by their reaction with silver and are prone to short circuit via zinc in battery tests (4)(5).

(2) Methyl cellulose formulations with carboxylic polymers allow minimal passage of silver but resist oxidation by silver oxide. These membranes have been found to resist catastrophic termination in battery tests. (4)(5).

(3) The S-type film was intermediate in that it picked up only small amounts of silver but also allowed silver to pass through it at only a very small rate. Cell tests of this film have been unsatisfactory because of the development of high internal resistance.

Calculations were made in the First Quarterly Report to show that the rate of silver migration through C3 film is too slow to deplete the silver significantly during cell life. However, new work has shown that the facts are different when the cells are stored in a charged condition for several months. There is then a deterioration in capacity, sometimes even a "soft short", attributable to silver passage through the membrane. This situation may be remedied by the use of C3-type membranes in conjunction with PVALc-type membranes, in separate wraps or as a laminate (See #5 film). Experiments along such lines are in progress.



#### F. Methacrylate-Acrylate Copolymers as Membranes

The methacrylate esters and their polymers are extremely resistant to hydrolysis by alkalies. An attempt was made to arrive at a copolymer structure of methacrylate ester and acrylic acid or acrylic ester which would give films of the desired physical and electrical properties. The rationale in the case of the copolymer ester was to hydrolyze the readily hydrolyzable acrylic ester moiety to give the requisite polarity for the needed low electrolytic resistance of the silver/zinc cell. No satisfactory membrane emerged from this program. Several copolymers of butyl methacrylate-acrylic acid (by hydrolysis of the copolymer esters) gave low resistance on a supporting Dynel cloth but were too brittle in the unsupported form. The supported films were not tested in cells because supported polyacidic compositions have been extensively investigated elsewhere.

Detailed description of the synthetic methods and results may be found in the First Quarterly Report pp 17-20, Second Quarterly Report pp 9-14.

#### G. Ethylene Copolymers with Acidic Constituents

A number of ethylene copolymers with acid groups or ester groups hydrolyzable to acid groups were investigated. Source of the starting polymers included developmental as well as commercial products. No entirely satisfactory membranes combining the properties of strength, flexibility and conductivity were produced. (First Quarterly Report p 22).

#### H. Derivatives from Chlorophosphonation of Polyolefins

The objective of this synthesis was similar to the above, to produce a heat-stable polymer of polyethylene or related backbone containing sufficient acidic groups for good conductivity. The chlorophosphonation reaction, a reaction of phosphorous trichloride and oxygen results in replacement of hydrogen of hydrocarbons or hydrocarbon polymers by phosphonyl dichloride groups,  $\text{POCl}_2$ . These are readily hydrolyzable to phosphonic acid. The most satisfactory polyolefin was EPR and the degree of chlorophosphonation required for low resistance in 30% KOH was found to be between 7 and 9% phosphorus content in the polymer. These polymers could be molded to films but not cast since no complete solvent could be found. At this level it was found that the polymers were difficult to reproduce. Work in this area was suspended because the process appeared impracticable for the scale required for producing film in quantity. (First Quarterly Report pp 25-28).

#### I. Unusual Cellulose Derivatives

This group of polymers included several commercially new derivatives of cellulose of mixed functionality as for example carboxymethyl hydroxymethyl cellulose and development products, not now commercial such as low degree of substitution methyl cellulose and carboxymethyl cellulose. These were procured through courtesy of the Dow and Hercules Corporations. Among new commercial cellulose, Ethulose, an ethyl hydroxyethyl cellulose (Chemaster Corp.) was of greatest interest. It was used in one of the films tested in cells at Burgess, #8 (p. 27). Other formulations are described in the Second Quarterly Report, p. 5.

#### J. Carboxymethyl Methyl Cellulose

Methyl cellulose shows excellent stability in electrolyte saturated with silver oxide but is not quite conductive enough to be used in itself as a membrane. With the objective of increasing the polarity of the commercial product a series of experiments was carried out in which the residual hydroxyls were converted to carboxy methyl groups,  $-OCH_2COOH$  by reacting with sodium chloroacetate. The conductivity was greatly improved by the reaction although results were somewhat obscured by the presence of co-products in the preparations. Details of the investigation may be found in the Second Progress Report, pp. 7, 8.

#### K. Modification of Methyl Cellulose/Polyacid Films with Polar Polymers

In moving to a higher polyacid content in methyl cellulose/polyacid combinations to improve conductivity, increased brittleness results. Attempts in ameliorating this included the addition of compatible polar polymers which might impart plasticity without at the same time detracting from conductivity. Materials studied were polyvinyl alcohol, hydroxyethyl cellulose and polyethylene oxide Polyox (Union Carbide). The plasticization effect was not as great as anticipated, the "plasticizing" polymer sometimes leading to greater brittleness. This was particularly true with Polyox. Several combinations with hydroxyethyl cellulose and polyvinyl alcohol showed marginally good flexibility (500-1000 flexes), and three of these formulations were prepared as membranes for cell tests at Burgess (Films 7, 9, 13). This phase of the work is discussed in more detail in the Second Quarterly Report, pp. 2-6.

#### L. Modification of Methyl Cellulose/Polyacid Films with Bases

The addition of inorganic bases to methyl cellulose/polyacid formulations has much the same effect as the addition of amines, that is, the resistance is lowered in proportion to the amount of base added. Whether this results likewise in extraction to leave a more open film has not been determined.

Calculations show that in the small volume of electrolyte used in cells the unneutralized polyacid materially lowers the alkali concentration. For this reason it would be desirable to include some KOH in the formulation. It has been found difficult, however, to procure good films of these formulations due to a tendency of the films to shrink and develop fissures during drying. Further work in this area is recommended. Films of this class are described in the Second Quarterly Report, pp. 3, 5.

#### M. Performance of Cells Constructed with Experimental Membranes

During the current contract selected experimental membranes were prepared in sufficient quantity for the construction of silver-zinc cells by the Burgess Battery Co. These were the 10 ampere hour nominal capacity SS 5.5 cells described in the First and Final Reports of the previous Contract NAS 5-3467 (4). Electrodes had a single layer per plate side of a Dynel separator, Webril 1401 and were U wrapped with five folds of the experimental membranes, which were 1.5 mils in thickness, except #13 membrane which was 1.2 mils and cellophane which was 1.0 mil.

Cells were charged at C/20 rate to 120% of previous discharge capacity and discharged at C/4 rate to 1 volt. In the third and fourth discharges the rate was C/1. Cycling was continued to failure by shorting or until an adequate picture of performance had been obtained. Tests on some of the membranes were unfinished at termination of the sub-contract.

Results are summarized in Table XI and in the appended Figures 1 to 18, which should be referred to in the discussion which follows.

### C3 Modifications

Under the previous contract, NAS 5-3467, one of the most promising membranes was found to be C3. This designation denotes a composition of 30 per cent poly(vinyl methyl ether/maleic anhydride) in a methyl cellulose base. Two preparatory modifications of this composition were tested. Film No. 3 (Figure 3) was prepared following a procedure to remove incompletely dispersed solid matter which is normal to commercial methyl cellulose. This material, which contributed to a slight opacity, is low degree of substitution methyl cellulose. It was largely removed by centrifugation of dilute solutions followed by re-concentration under vacuum. The performance as shown by Figure 3 was, if anything, somewhat inferior to C3 prepared in the conventional manner (Figure 2). As shown in Table X the physical and electrical properties were similar.

A second C3 modification C3L film #4 was made by casting a thin film of C3 on top of a previously dried thin film to give, in effect, a laminate. The rationale here was to minimize the possibility of defects such as pinholes. As shown in Figure 4 performance was essentially the same as the control C3 film of Figure 2.

The C3 films of Figures 2, 3, 4 all showed good cycle life without shorting. However, it should be noted that discharge capacity history was far lower than in tests made under the previous contract both at Burgess and in follow-up tests at NAD Crane (5). This is illustrated in Figure 2 where the discharge history curve of the 1964 test is superimposed on the graph of the current tests. The reason for this discrepancy is not understood at this time. It should be noted also that the present performance of the control cellophane of Figure 1 was considerably better than in the 1964 tests when shorting resulted after respectively 14, 15, 17 and 20 cycles. This is illustrated by the superimposed curve of one of the 1964 tests on Figure 1.

#### Triple Laminate Film #5

This film was prepared by multiple casting of three 0.5 mil films. The first and third layers were C3, the middle 0.5 layer was a casting of polyvinyl alcohol, 98% hydrolyzed. The rationale here was to provide in a single membrane a composition which resisted both zinc penetration (C3) and silver penetration (polyvinyl alcohol). As seen in Figure 5 these cells showed higher initial discharge capacity than the C3 films, and a good cycle life. The precipitate drop in capacity indicated incipient shorting. Further testing is recommended.

#### Film #6

This membrane was developed to operate at concentrations of KOH higher than 30%. As seen in Table XI the electrolytic resistance in 45% KOH was considerably lower than for a C3 film. The composition amounted to a C5 film containing 20% polyvinyl alcohol. The latter was included as a plasticizing component and as a possible silver stopper. Cells for this membrane were tested in 40% KOH as shown in Figure 13. Capacity was 85 and 100% of nominal after the nineteenth discharge when tests were discontinued. Further study of this type membrane is recommended.

#### Film #8

This composition was based on the incorporation of 20% polyvinyl methyl ether/maleic anhydride in Ethulose (Chemaster Corp.) an ethyl cellulose containing some hydroxyethyl groups. Cells were tested in both 30% (Figure 6) and 40% (Figure 14) KOH. One cell shorted in each test while the duplicate cells showed possibility of fairly extended life. However, both were well below nominal capacity throughout.

#### Film #9

This composition achieved higher conductivity by substituting hydroxyethyl cellulose for 30% of the methyl cellulose in C3. Cells shorted after brief cycle life in both 30% and 40% KOH. (Figures 7 and 15).

#### Film #10

This composition achieved higher conductivity by inclusion of 3-hydroxypropylamine in C3. As shown in Figure 15, cells in 40% KOH shorted after 20 cycles.

#### Film #11

This composition achieved higher conductivity by inclusion of 3-hydroxypropylamine in B5. Poor cycle life in 40% KOH ended in shorting, as shown in Figure 17.

#### Film #12

This film was methyl cellulose cast from aqueous solution containing 6 parts KOH per 100 of polymer. Tests in 30% KOH, as shown in Figure 8, were carried through 37 cycles before discontinuation. Performance was similar to C3 for most of the period studied, but appeared somewhat erratic in the latter cycles. Further study of this type of film is recommended.

#### Film #13

This composition achieved improved conductivity by inclusion of 3-hydroxypropylamine with C2. Tests in 30% and 40% KOH are summarized in Figures 9 and 13. Cells shorted at the fifteenth cycle in 30% KOH and showed low capacity and erratic behavior in 40% KOH after the 20th cycle..

Table XI

## Life Cycle Tests Burgess SS 5.5 10 A.H. Cells

Membrane No. 5-9107-	2	3	4	5	6	8
Composition	C3	C3C	C3L	3L	GIM	GE
Lot No.	445- 104	436- 137	445- 98	445- 105	485- 71	485- 109
Thickness, mils	1.5	1.5	1.5	(X)	1.5	1.55
Swollen Wt./Dry Wt.						
30% KOH	1.6	1.6	1.6	2.12	3.1	2.0
40% KOH	1.7	1.7	1.7	2.04	2.3	1.8
Resistance, 45% KOH - milliohms-in. <sup>2</sup>	357	430	343	213	45	185
MIT Flex 200 g tension cycles	889	593	561	10,000	1137	1716
Ag <sub>2</sub> O Oxide in 30% KOH (Y)						
Original A      psi	2510	3250	2760	496	898	2440
Final B        psi	2160	3180	2790	382	568	1570
B/A	.86	.98	1.01	.77	.65	.64
Cycle Life 30% KOH						
Capacity at 10th cycle avg. A.H.	6.6	5.6	6.8	11.4	-	7.3, 0
15th cycle avg. A.H.	6.3	5.2	6.5	11.7	-	7.2, 0
20th cycle avg. A.H.	6.5	5.0	6.1	9.0	-	7.3, 0
Terminated at Cycle #	66	66	66	66	-	37
Capacity at last cycle avg. A.H.	4.4					5.3, 0
Termination Cause	L,U	L,U	L,U	L,U	-	U, S
Cycle Life 40% KOH						
Capacity at 10th cycle avg. A.H.	11.5	10.7	-	-	9.8	6.0, 0
15th cycle avg. A.H.	12.4	11.7	-	-	9.6	6.2, 0
20th cycle avg. A.H.	8.8	6.6	-	-	-	6.7, 0
Terminated at Cycle #	66	66	-	-	19	37
Capacity at last cycle avg. A.H.	2.5	2.7	-	-	9.4	4.5, 0
Termination cause	L, U	L, U	-	-	U	U, S

Notes: (X) Irregular surface. Probably avg. 1.5 mils.  
L Low ampere hours  
U Unfinished (not yet shorted)  
S Shorted  
Y Films stirred 3 days at 72° F.



Table XI (CONTINUED)

Life Cycle Tests Burgess SS 5.5 10 A.H. Cells						
Membrane No. 5-9107-	9	10	11	12	13	PUDO
Composition	AHM	C3 + HPA	B5 + HPA	MC KOH	C2 HPA	Cello- phane
Lot No.	485- 111	499- 30	499- 31	499- 33	499- 137	
Thickness mils	1.55	1.55	1.5	1.5	1.2	1.0
Swollen Wt./Dry Wt.						
30% KOH	1.7	1.7	2.0	1.33	1.52	2.9
40% KOH	1.7	1.7	2.0	1.28	1.51	2.6
Resistance 45% KOH - milliohms-in. <sup>2</sup>	57	0	31	287	12	30
MIT Flex 200 g tension cycles	277	363	970	4465	8501	10,000+
AgO Oxide in 30% KOH (Y)						
Original A psi	725	1700	725	4570	2630	3130
Final B psi	639	1590	759	4560	2560	457
B/A	.88	.94	1.04	1.00	.98	.15
Cycle Life 30% KOH						
Capacity at 10th cycle avg. A.H.	0	-	-	8.8	8.0	11.5
15th cycle avg. A.H.	-	-	-	7.5	0, .30	10.3
20th cycle avg. A.H.	-	-	-	8.5	-	8.4
Terminated at Cycle #	-	-	-	37	15	50
Capacity at last cycle avg. A.H.	0	-	-	4.5	0, .3	1.8
Termination Cause	S	-	-	L,U	S	L,U
Cycle Life 40% KOH						
Capacity at 10th Cycle avg. A.H.	4.8	5.0	5.9, 0	-	8.0	12.7
15th cycle avg. A.H.	3.2	5.1	1.6, 0	-	5.4	12.1
20th cycle avg. A.H.	0, .5	-	-	-	4.8	6.7
Terminated at Cycle #	20	19	8, 19	-	37	86
Capacity at last cycle avg. A.H.	-	4.5	0	-	4.5	3.5, 0
Termination cause	S	L,U	S	-	L,U	L,S

Notes: (X) Irregular surface. Probably avg. 1.5 mils.

L Low ampere hours

U Unfinished (not yet shorted)

S Shorted

Y Films stirred 3 days at 72° F.

The compositions of the membranes in Table XI are identified as follows:

(C3) = 7 parts methyl cellulose/3 parts PVMMA; (C3C) = (C3) prepared from centrifuged methyl cellulose solution; (C3L) = double casting of C3; (3L) = triple coating C3/PVALc/C3; (GLM) = 4 parts PVMMA/2 parts PVALc/4 parts methyl cellulose; (GE) = 2 parts PVMMA/8 parts Ethulose; (AHM) = 3 parts polyacrylic acid/3 parts hydroxyethyl cellulose/4 parts methyl cellulose; (C3 + HPA) = C3 plus 10% (on polymer) of 3-hydroxypropylamine; (B5 + HPA) = 5 parts polyacrylic acid/5 parts methyl cellulose/0.1 part 3-hydroxypropylamine; (MCl5-KOH) = methyl cellulose containing 6% KOH; (C2 + HPA) = C2 plus 10% of 3-hydroxypropylamine.

Comparison of 30% vs. 40% KOH in Cells:

In the cell tests of the present report, cellophane showed longer cycle life in 40% KOH than in 30% KOH. This is in agreement with observations made elsewhere (reference 7, page 91) and with the experimental fact that 40% KOH, which dissolves less silver oxide than 30% KOH, degrades cellophane less rapidly. (reference 4, pages 23, 24).

The higher ampere-hour capacity of C3 membranes in 40% KOH (figures 2, 3, 4, 11, 12) of present report is difficult to reconcile with the higher resistance of C3 in 40% KOH as well as with previous behavior of C3 in 40% vs. 30% KOH at N. A. D. Crane (reference 5, Figures 10, 11 and Table 5). In the Crane tests it was found that both C3 and B3 membranes showed lower capacity in 40% KOH than in 30% KOH.

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5) T. J. Hennigan, Separator Materials for Silver Oxide Zinc and Silver Oxide Cadmium Electrochemical Cells, Goddard Space Flight Center X-716-65-331 (1965).

6) H. L. Pfluger and H. E. Hoyt, Contract NAS 5-9107, Second Quarterly Report 1965.

7) John Rhyne, Jr., Silver Oxide-Zinc Battery Program, Delco Remy Division of General Motors, WAD Technical Report 61-31 (1961).

## ITEMS OF NEW TECHNOLOGY

### A. IMPROVED TECHNIQUE FOR MEASUREMENT OF SILVER ION DIFFUSION THROUGH FILMS

Improvements have been made in the radioactive tracer procedure for studying the diffusion of silver (argentate) ions through films in strong alkaline solutions. By using glass rather than acrylate resin for construction of the cell, silver losses on cell wall are avoided. Gaskets and other plastic parts contacting the silver solution also were restricted to materials not reactive with alkaline silver solution. Among the materials found satisfactory were polyethylene and Teflon.

Cf. pp. 17, 18, 19 of this report; also Conclusion (1).

### B. SILVER ION DIFFUSION vs. Ag-Zn CELL PERFORMANCE WITH METHYL CELLULOSE/POLYACID FILMS

Films composed of methyl cellulose intimately mixed with high-molecular polyacids, such as polyacrylic acid or the copolymer of vinyl methyl ether and maleic anhydride, have in repeated tests resisted oxidative attack and physical degradation under the chemical conditions of the alkaline silver-zinc battery cell. Studies with radioactive silver (argentate) ion have shown that these films reduce only minimal quantities of silver ion to metallic silver, but they permit small quantities of silver ion to diffuse through them. Films of this type have resisted catastrophic termination in cell tests.

Cf. pp. 17-19, 24, 26; also Conclusion (2).

### C. SILVER-ION DIFFUSION vs. Ag-Zn CELL PERFORMANCE WITH HYDROXYL-CONTAINING SEPARATOR FILMS

Certain films whose polymers contain hydroxy groups may be used to keep silver (argentate) ions from diffusing from silver electrode to zinc electrode in alkaline cells. This property arises from the power of the hydroxyl groups to reduce the silver ions to metallic silver. In addition to the commonly used cellophane, this class of materials includes a number of substances which are less drastically damaged by the reducing process. Among these stronger substances are polyvinyl alcohol, hydroxy polyvinyl alcohol (HEPVA) and hydroxy-ethyl cellulose-methyl cellulose films. In cell tests these materials have shown improved cycle-life over cellophane, but eventually the damage they suffer does result in short circuit, probably via zinc.

Cf. this report pp. 17-19; also Conclusion (3).

Cf. also Items E, F, G and J of New Technology under Contract  
NAS 5-3467

## ITEMS OF NEW TECHNOLOGY (CONTINUED)

### D. IMPROVEMENT OF METHYL CELLULOSE SEPARATOR FILMS WITH INORGANIC BASES

Films in which methyl cellulose is the sole polymer were improved about twenty-fold in conductivity in 45% KOH by depositing them from a solution containing six parts potassium hydroxide per hundred of methyl cellulose. Hydroxides of sodium, lithium, and barium may be similarly applied.

Cf. pp. 7-10, 25A, 27 and Fig. 8 of this report; also Conclusion (4).

### E. BATTERY SEPARATOR FILM FROM METHYL CELLULOSE CONTAINING ORGANIC SALTS

Improvement in conductivity (up to 100 fold) of methyl cellulose film was achieved by depositing from solutions containing salts of organic acids, in amount 10 to 30% by weight of polymers. Acids studied included formic, acetic, propionic, butyric, lactic and salicyclic. Films of this type possess improved flexibility even at low humidities, a property attributable to hygroscopicity of the salts. A formulation selected for further tests in cells is 90 parts, by weight, methyl cellulose, 10 parts PVM/MA and 28 parts potassium lactate.

Cf. pp. 13-16 of this report; also Conclusion (5).

### F. IMPROVING CONDUCTIVITY OF METHYL CELLULOSE BATTERY SEPARATOR BY PRESWELLING IN 15% KOH

Conductivity of methyl cellulose films in 45% KOH was improved about 100-fold by preswelling in 15% KOH. After exposure of preswollen film to stirred 45% KOH for seven days, the overall weight pick-up was 61% in contrast to only 22% when untreated methyl cellulose film was equilibrated directly in 45% KOH.

Cf. pp. 11 and 12 of this report; also Conclusion (6).

## ITEMS OF NEW TECHNOLOGY (CONTINUED)

### G. CARBOXYMETHYL METHYL CELLULOSE FOR BATTERY SEPARATOR USE

Exploratory synthetic experiments demonstrated that methyl cellulose can be chemically modified by replacing the hydrogen of the residual hydroxyl groups by carboxy methyl. Films were prepared which had conductivity improved about 20-fold over C3 (7:3 methyl cellulose/PVMA) in 45% KOH. Development of the synthesis on a commercial scale would entail considerable effort, however, and the advantages of the new product are not at present deemed sufficiently revolutionary to justify such effort.

Cf. page 21 of this report; also Conclusion (9).

Cf. Second Quarterly Report, pages 7,8.

### H. HYDROXYETHYL ETHYL CELLULOSE FOR BATTERY SEPARATOR USE

A commercial grade of hydroxyethyl ethyl cellulose (ETHULOSE) was found to have conductivity in alkaline solutions similar to methyl cellulose and silver ion reducing properties similar to hydroxyethyl cellulose. This polyfunctional material was also found to be compatible with polyacids in the same way as methyl cellulose. Tests in cells of a formulation with PVM/MA are in progress.

Cf. pages 21, 25, 26, Figures 6 and 14 of this report; also Conclusion (10).

### I. ETHYLENE-ACRYLIC ACID COPOLYMERS FOR BATTERY SEPARATOR USE

Preliminary evaluations of ethylene-acrylic acid copolymers indicate their potential usefulness in separator application, in that conductivities in the useful range were obtained. The polymers available thus far were too weak and brittle to be used as unsupported membranes.

Cf. page 20 of this report; also Conclusion (13).

Cf. First Quarterly report, page 22.

## ITEMS OF NEW TECHNOLOGY (CONTINUED)

### J. LAMINATE FILM FOR BATTERY SEPARATOR USE

A laminate has been made of a film of polyvinyl alcohol sandwiched between two layers of film formed from an intimate mixture of methyl cellulose with a polyacid polymer. A single laminate of the two types of film would curl and be difficult to handle. The triple laminate is conveniently handled and can be used to wrap electrodes for separator use in the alkaline Ag-Zn cell. Preliminary tests of a laminate of polyvinyl alcohol with a film composed of 7 parts methyl cellulose and 3 parts PVMMA in cells indicate long life-cycle with no catastrophic termination. In addition, the composite film promises to have superior constancy of performance after long periods of standing in the charged condition.

Cf. page 25 and Figure 5 of this report; also Conclusion (15)

APPENDIX OF FIGURES



Fig. 1

FUDO Cellophane Cells, NAS 5-9107  
30% KOH, Cycling Data

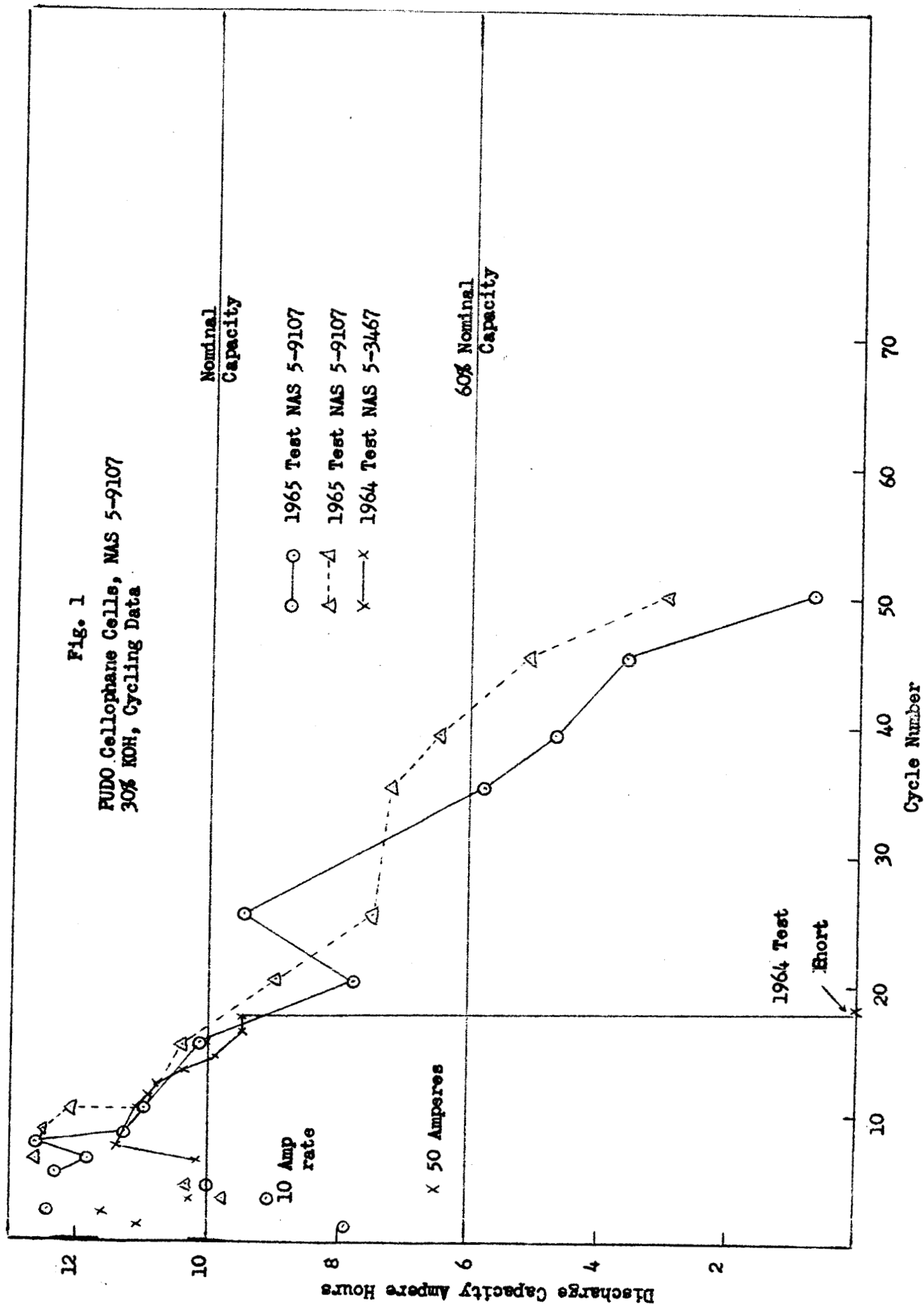


Fig. 2  
C3 Cells, NAS 5-9107-2  
30% KOH, Cycling Data

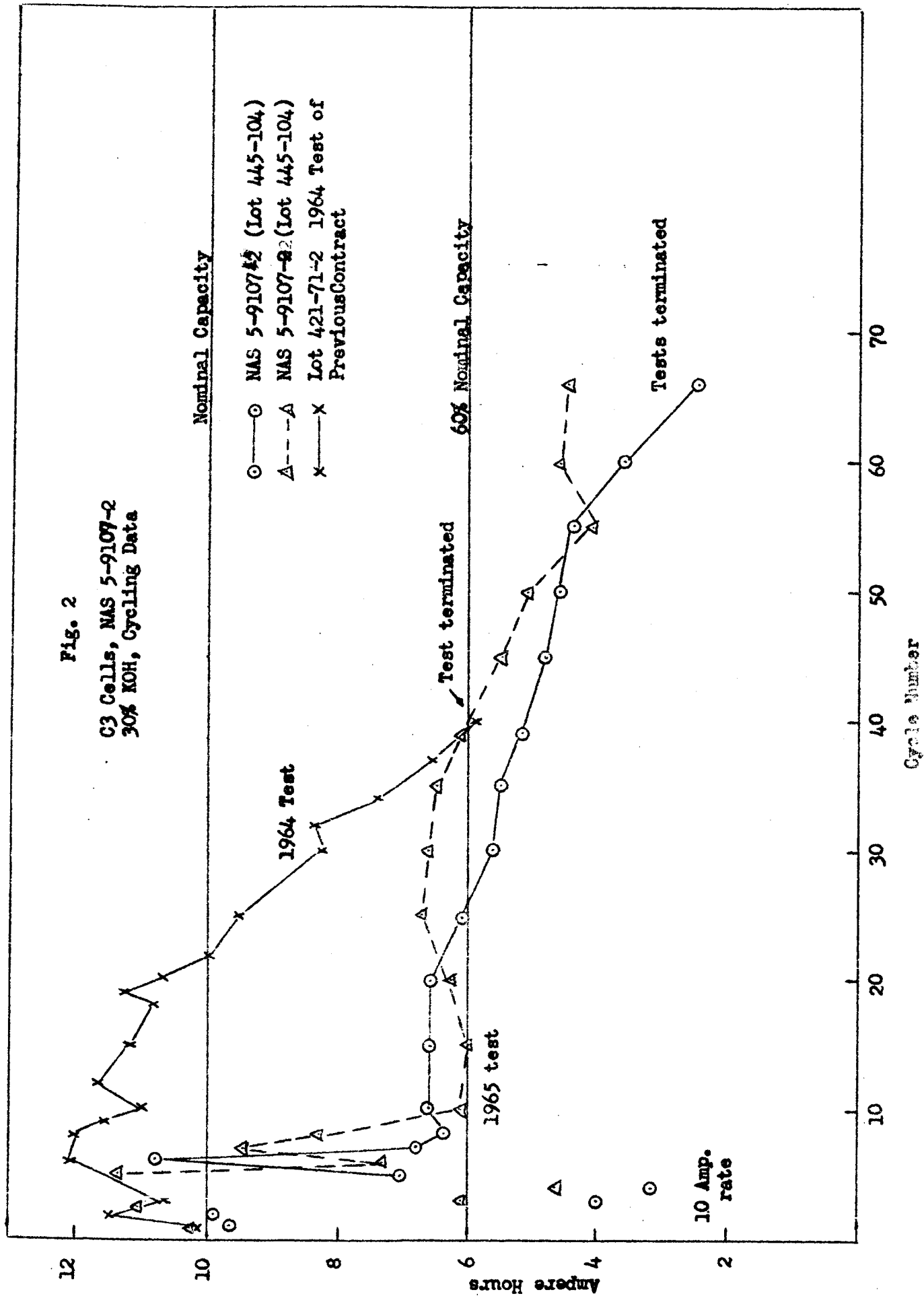


Fig. 3  
C3C Cells, NAS 5-9107-3  
30% KOH, Cycling Data

Nominal Capacity

60% of Nominal Capacity

Tests terminated

10 Amp.  
rate

Cycle Number

12

10

8

6

4

2

Discharge Capacity, Ampere Hours

10

20

30

40

50

60

70

○  
△

○  
△

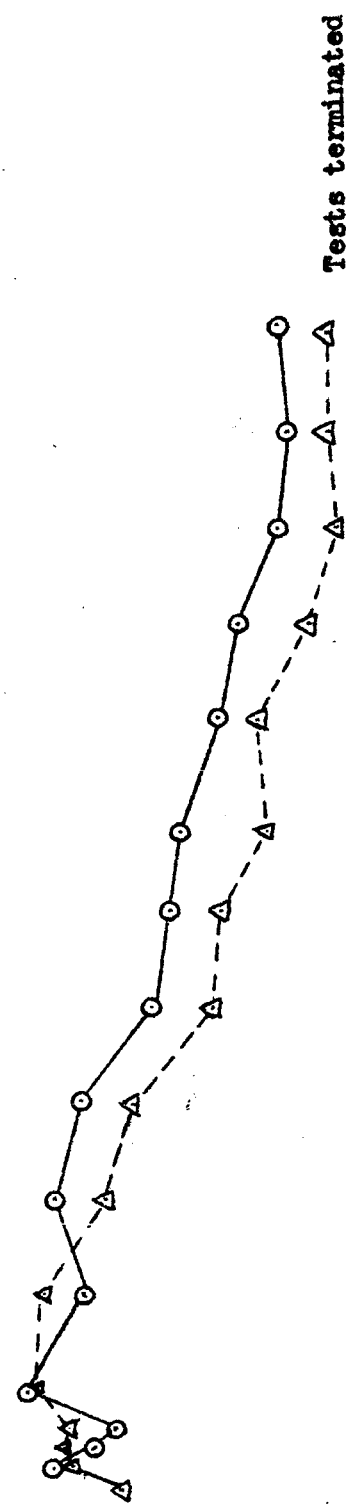


Fig. 4  
C3L Cells, NAS 5-9107-4  
30% KOH, Cycling Data

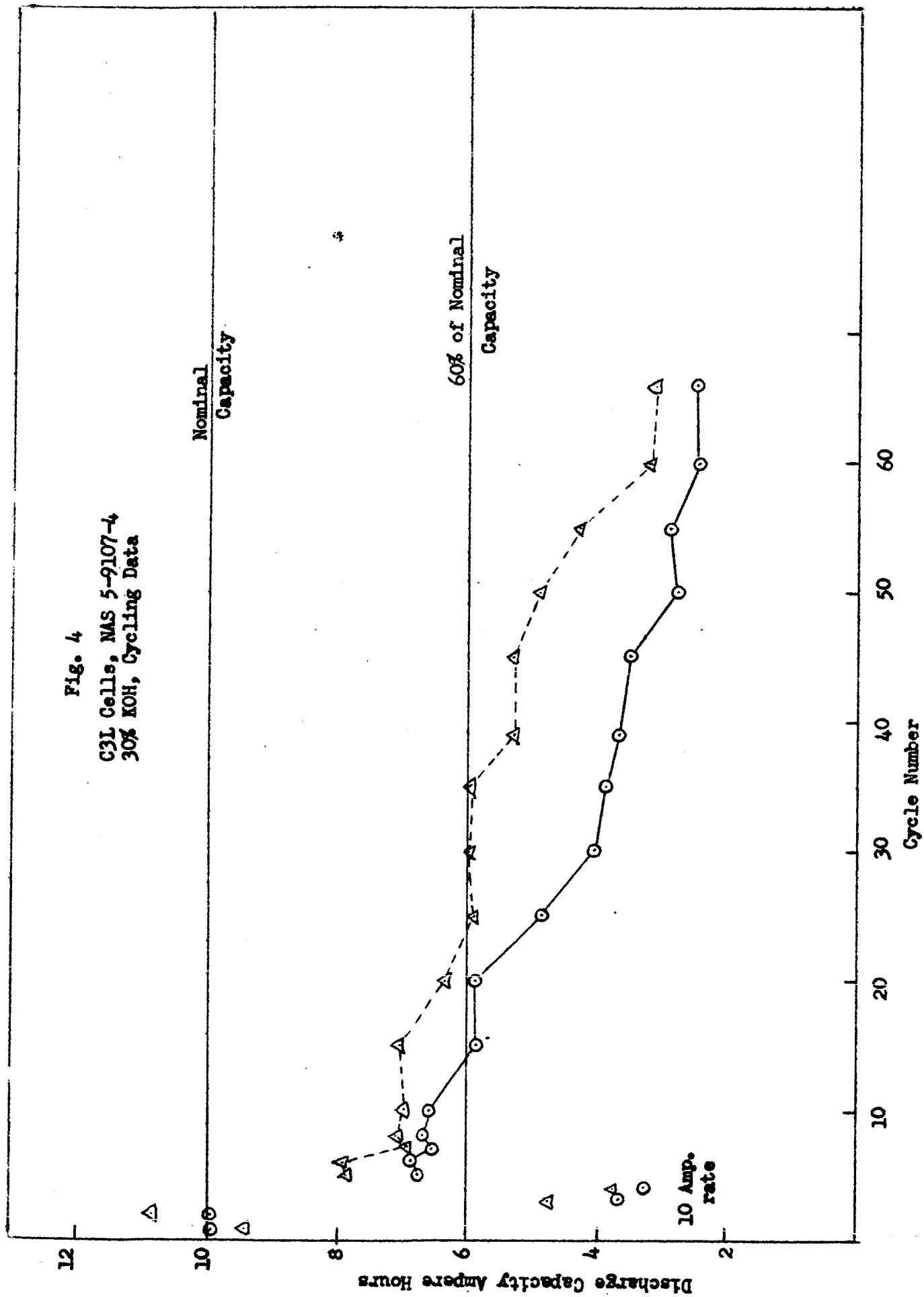


Fig. 5  
Triple Laminate Cells NAS 5-9107-5  
30% KOH, Cycling Data

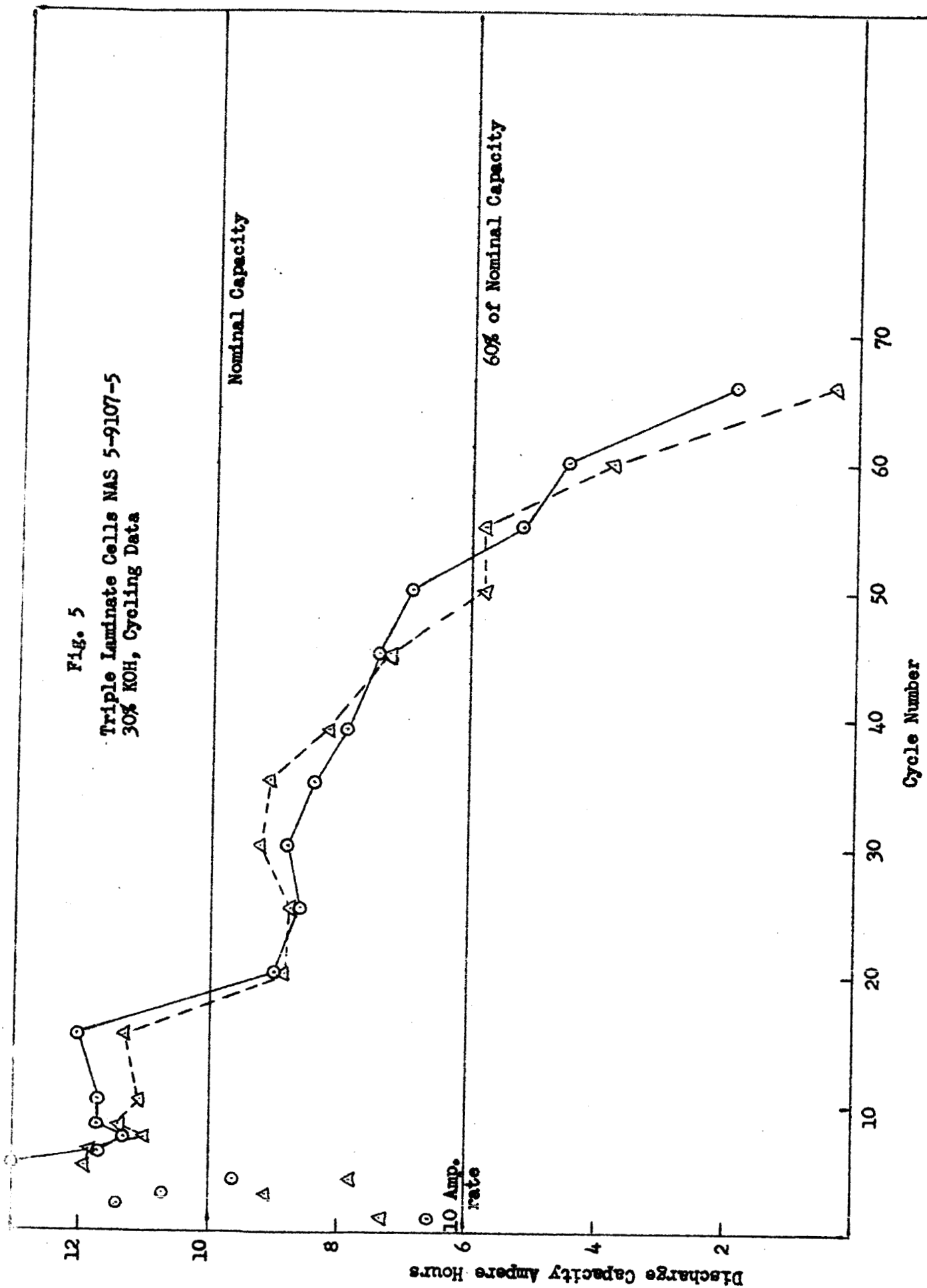


Fig. 6  
 PTFMA/Ethulose Cells NAS 5-9107-6  
 30% KOH Cycling Data

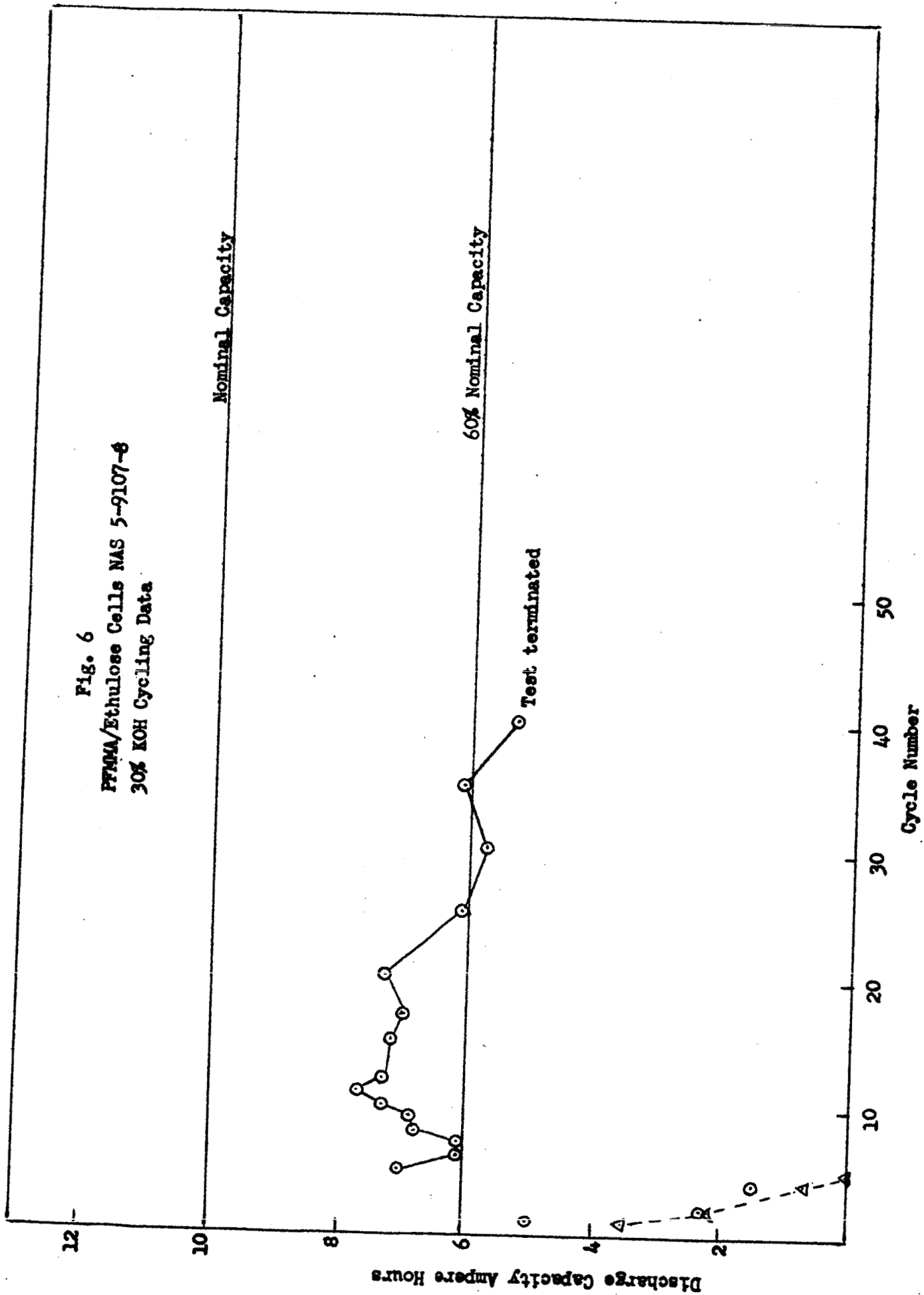


Fig. 7  
PAA/HEC/MC Cell NAS 5-9107-9  
30% KOH Cycling Data

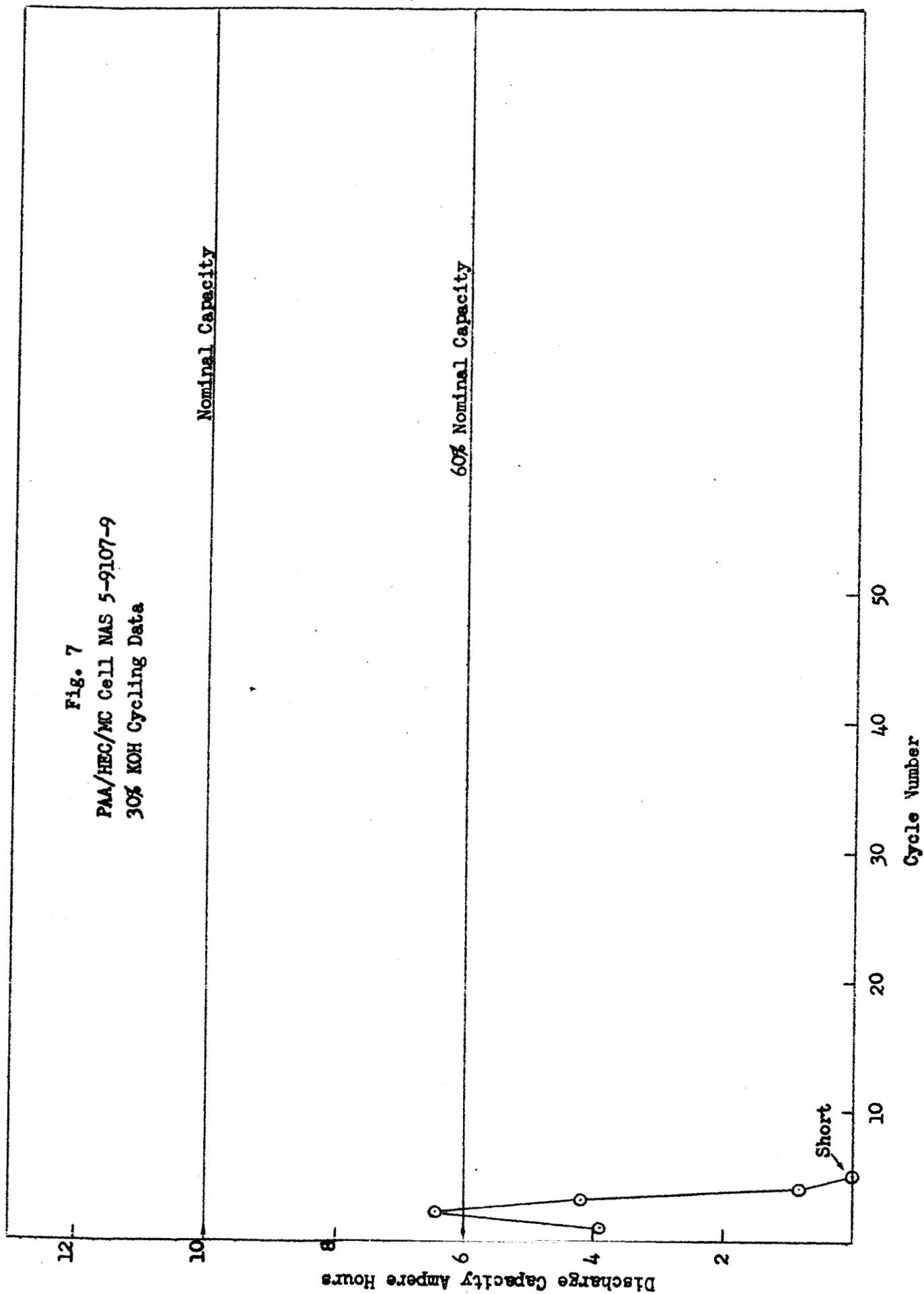


Fig. 8  
KOH/MC Cells NAS 5-9107-2  
30% KOH Cycling Data

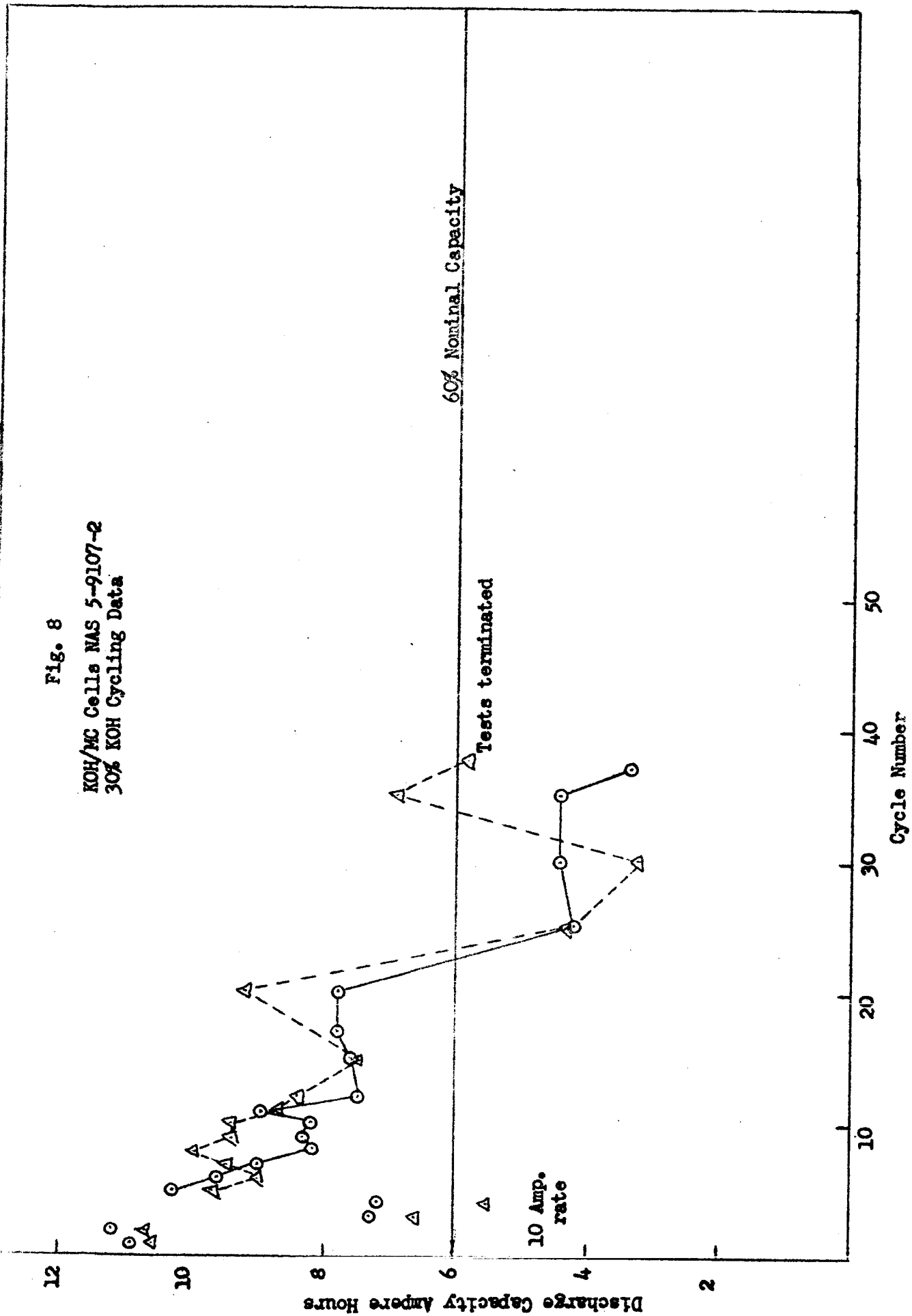




Fig. 9

C2 + 3-hydroxypropylamine Cells NAS 5-9107-13  
30% KOH Cycling Data

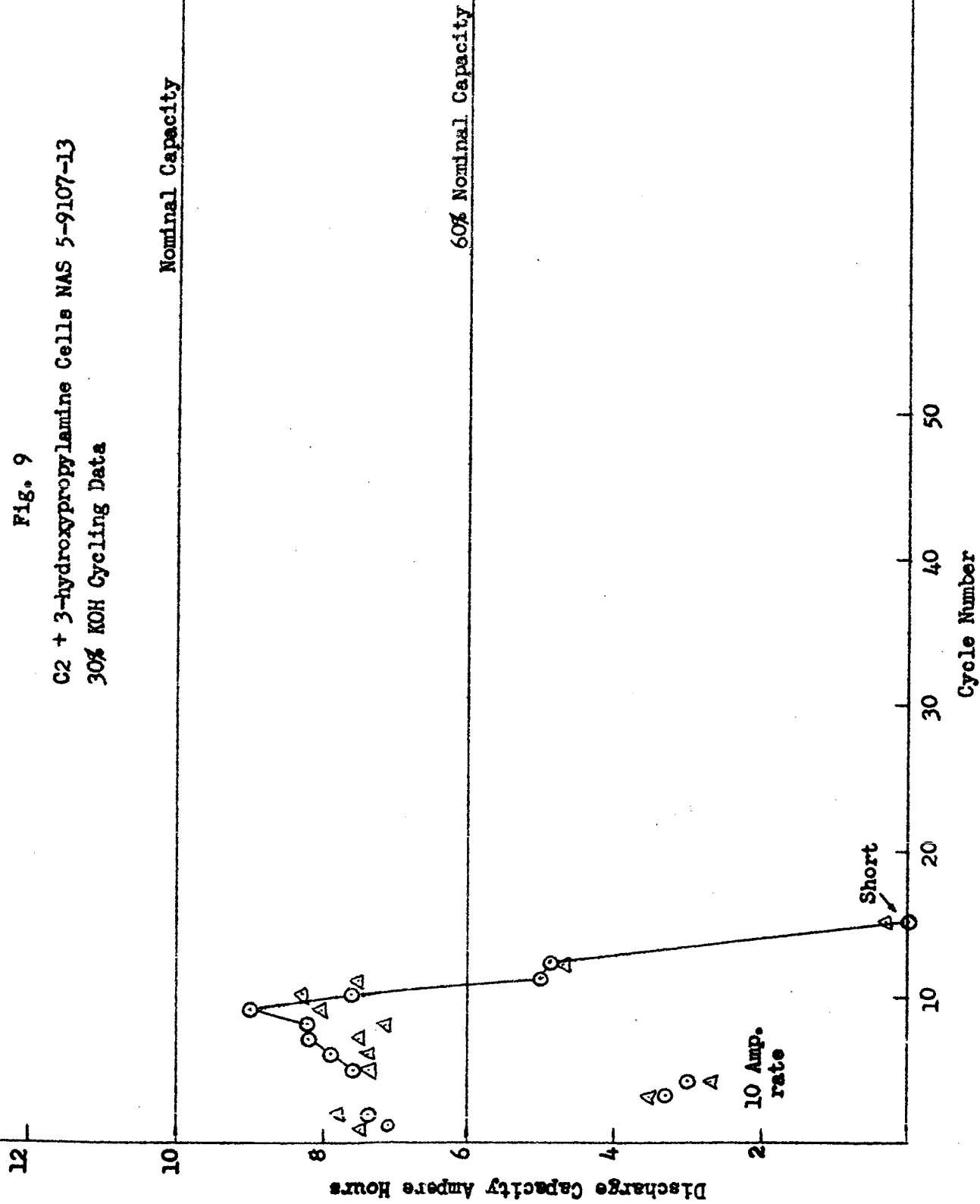


Fig. 10

PUDO Cellophane, NAS 5-9107  
40% KOH, Cycling Data

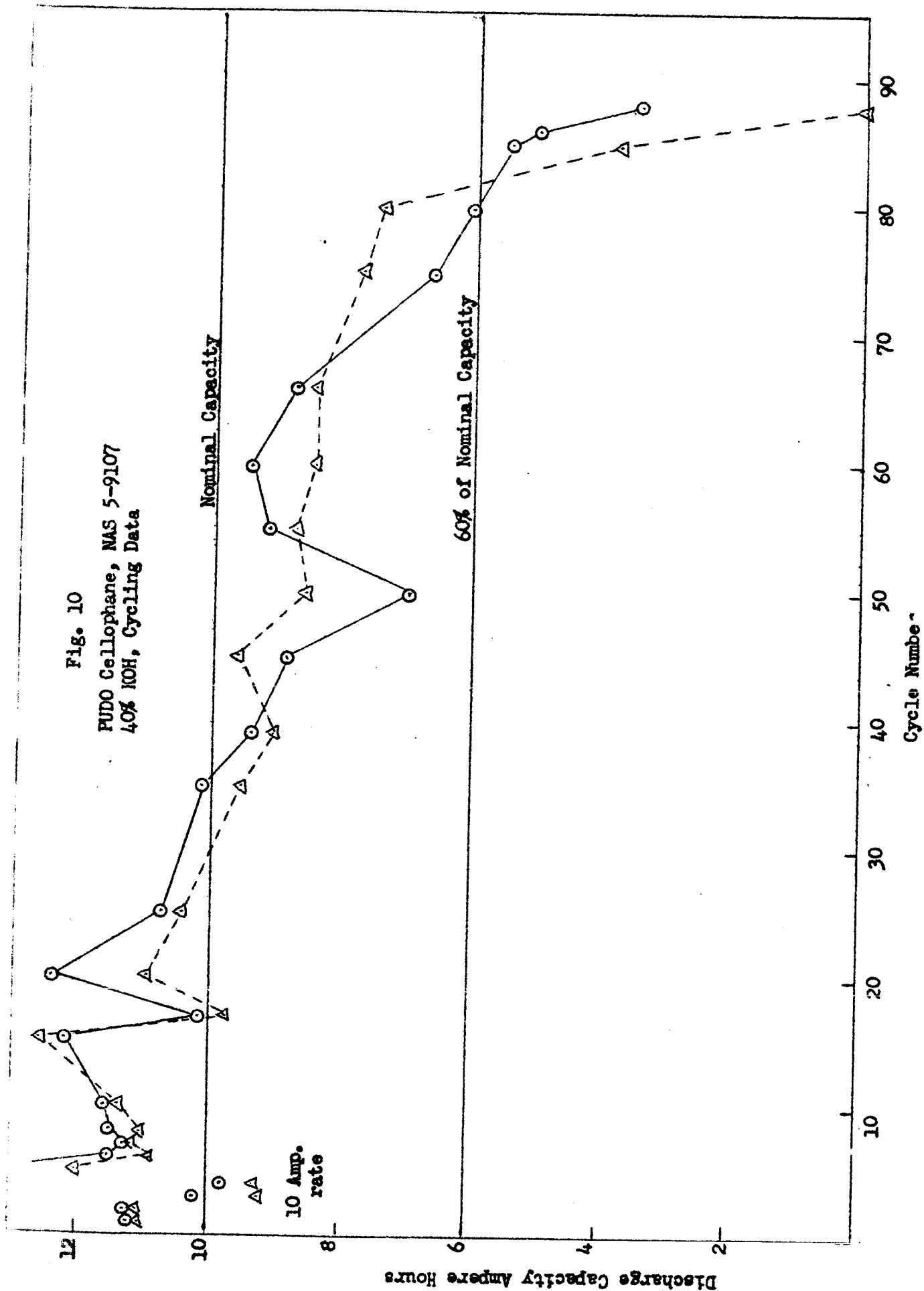


Fig. 11  
C3 Cells NAS 5-9107-2  
40% KOH, Cycling Data

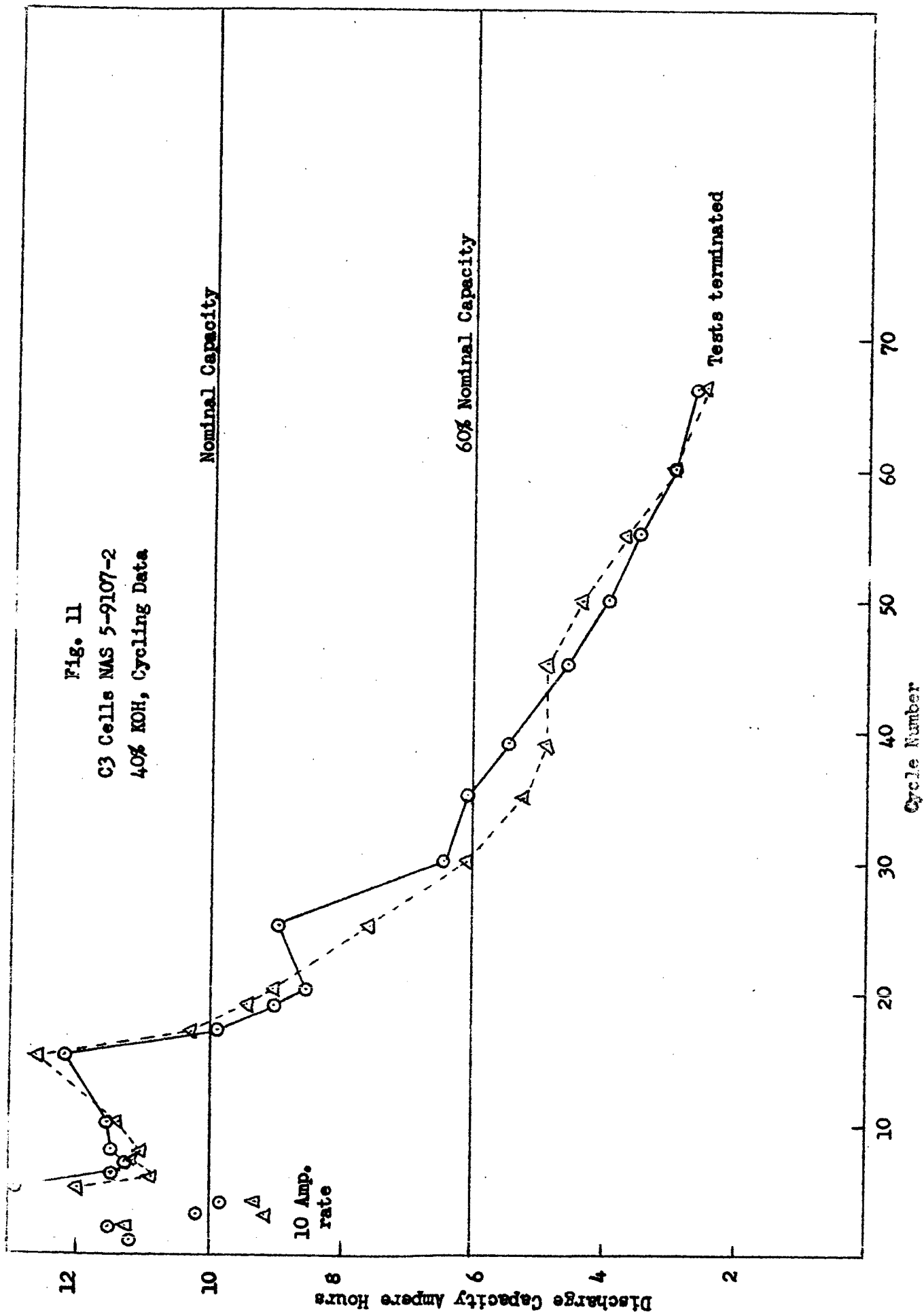


Fig. 12

C3C Cells, NAS 5-9107-3  
40% KOH, Cycling Data

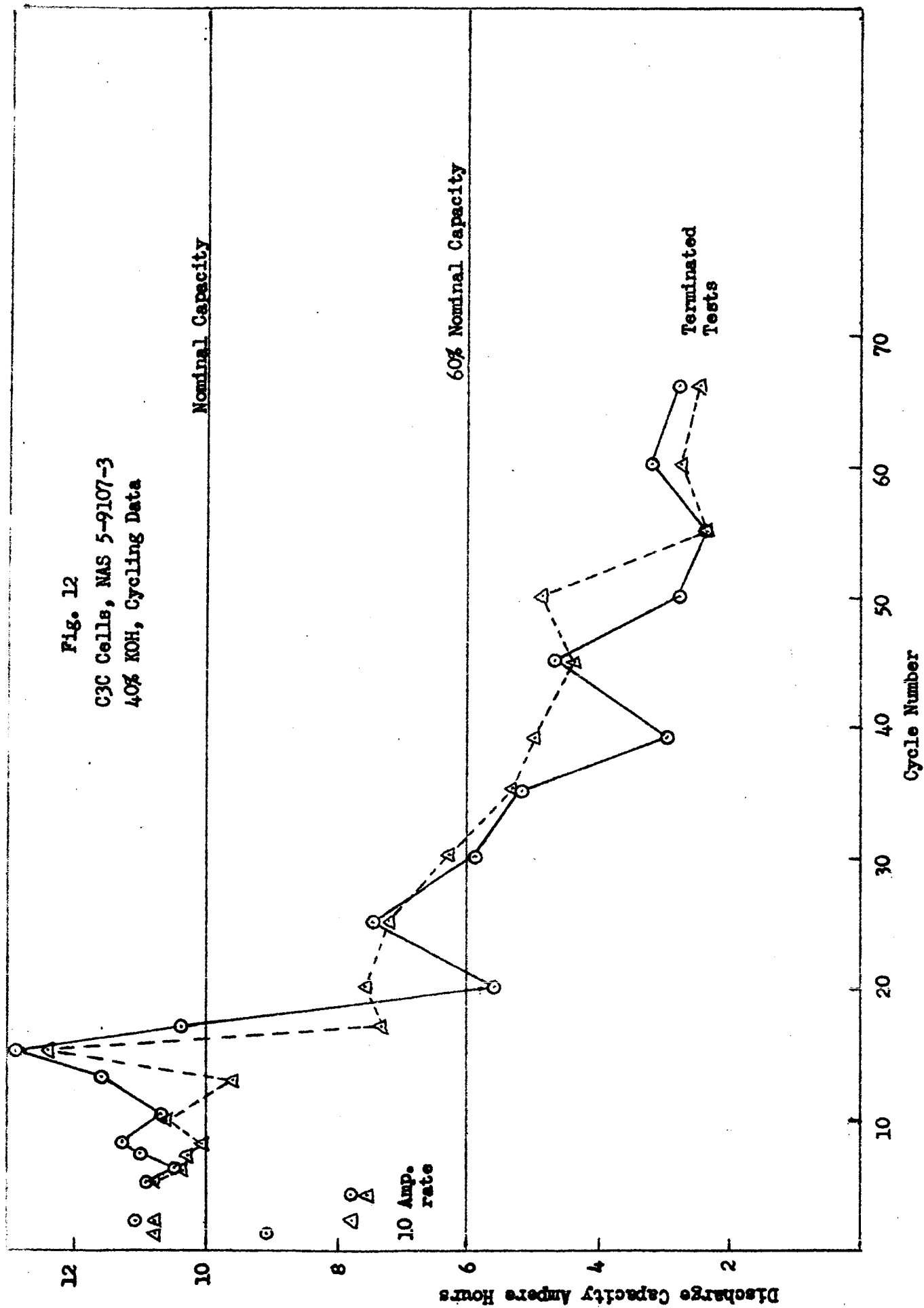


Fig. 13

PVDM/PAVA/PC Film NAS 5-9107-6  
40% KOH Cycling Data

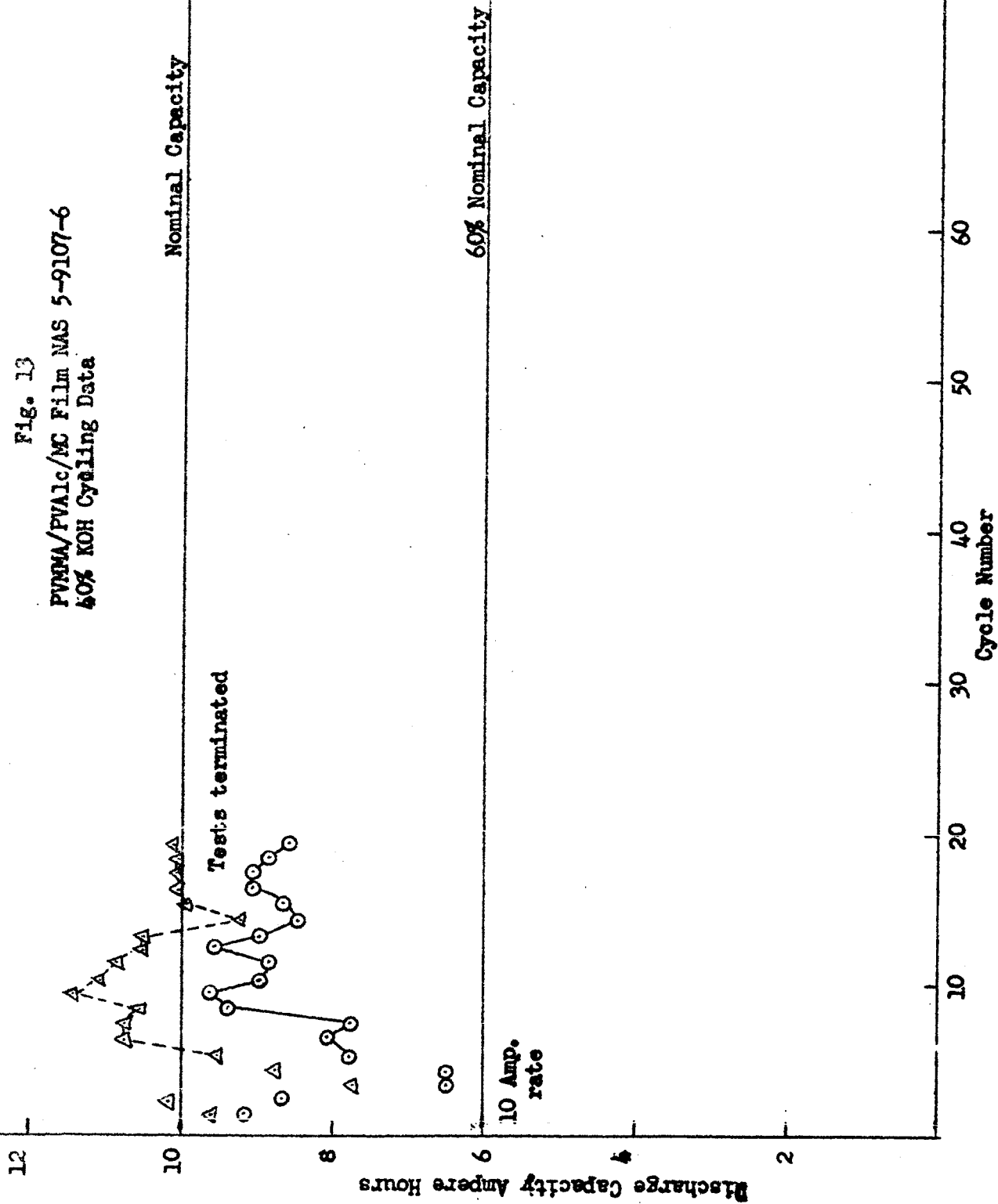


Fig. 14  
 PVMA/Ethulose Cells NAS 5-9107-8  
 40% KOH Cycling Data

Nominal Capacity  
 60% Nominal Capacity

Discharge Capacity  
 Ampere Hours

10 Amp.  
 Rate

Cycle Number

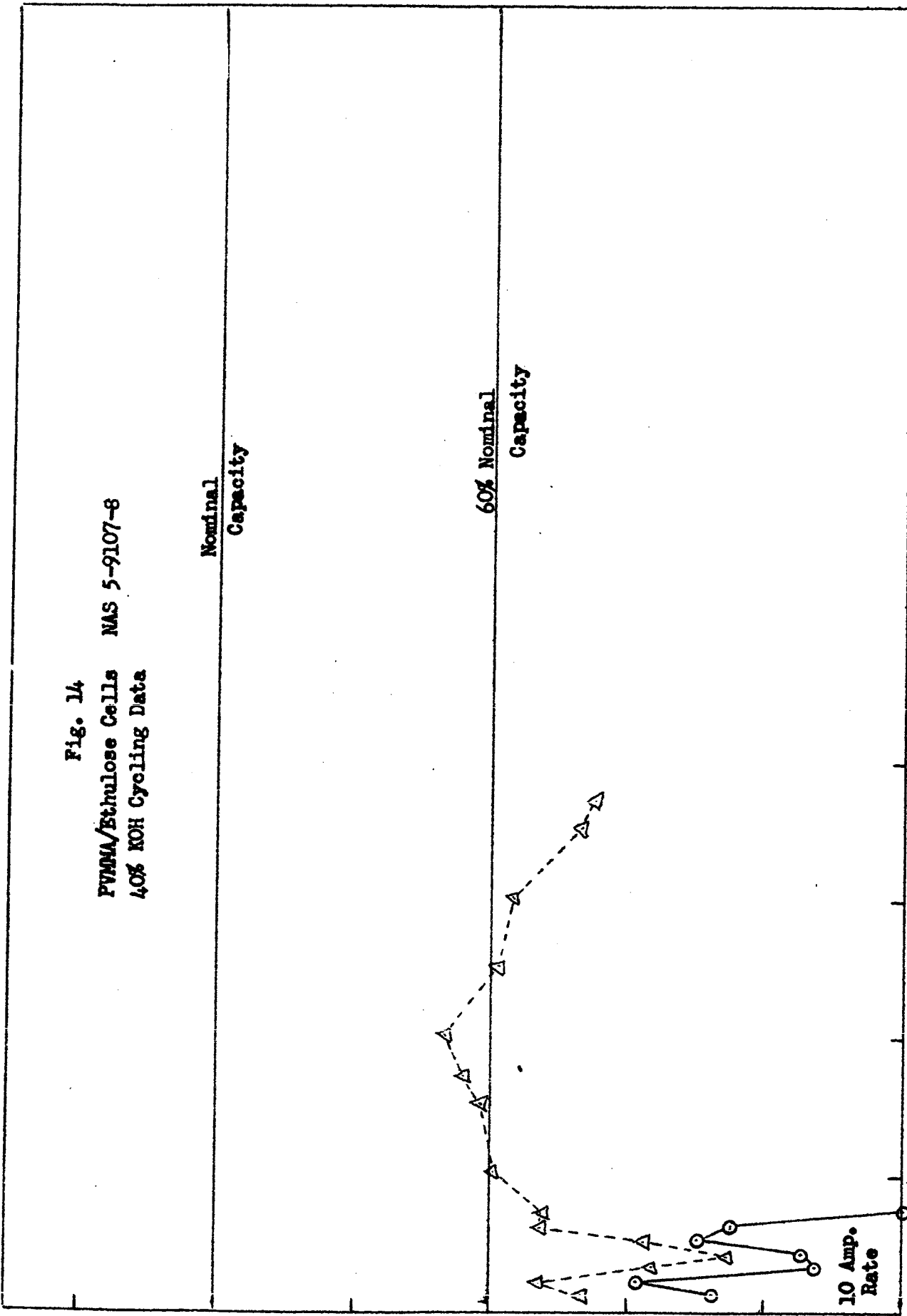


Fig. 15  
PAA/HEC/ME Cells NAS 5-9107-9  
4.0% KOH Cycling Data

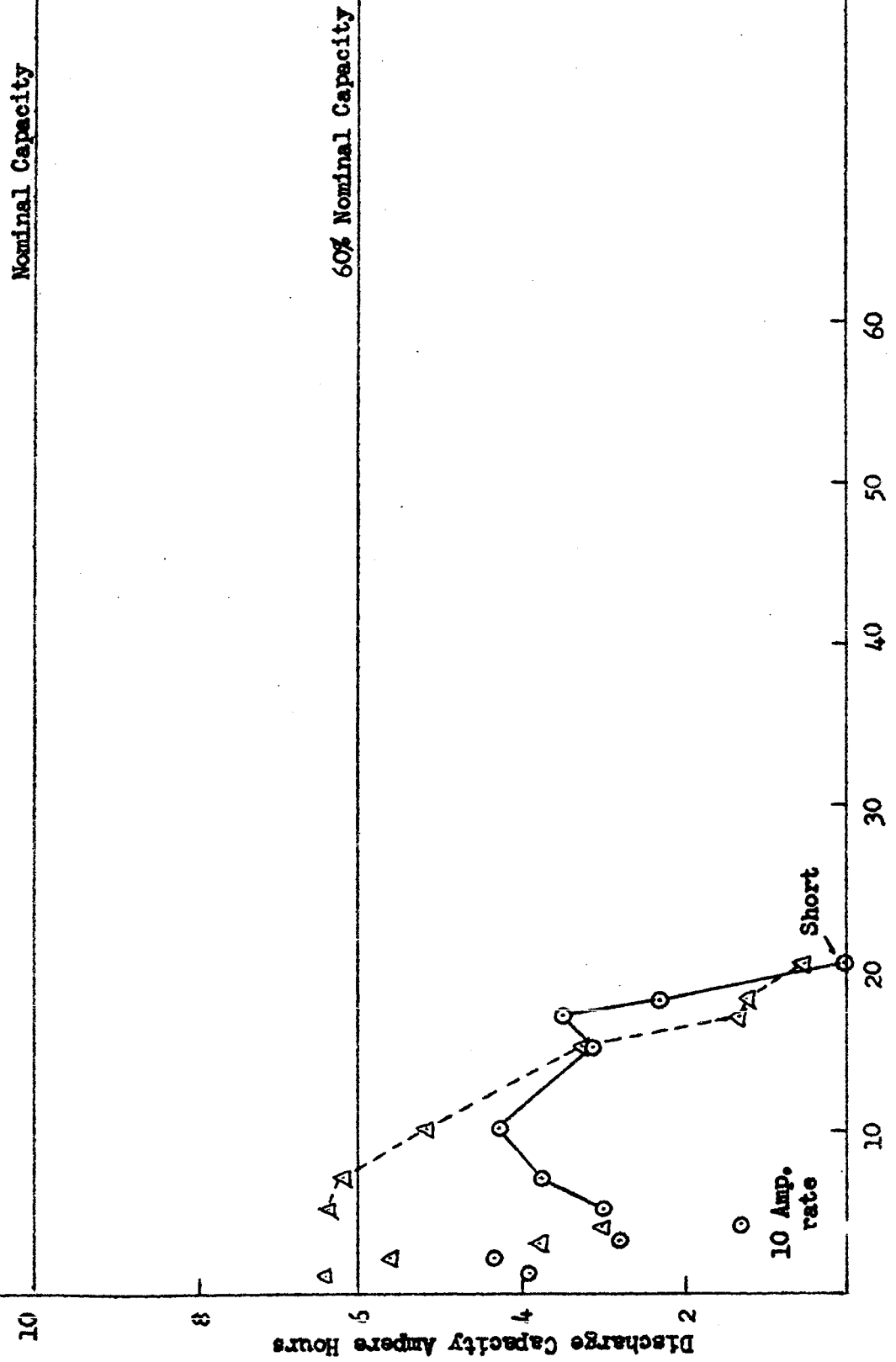


Fig. 16  
 3 + 3-Hydroxypropylamine Cells NAS 5-9107-10  
 40% KOH Cycling Data

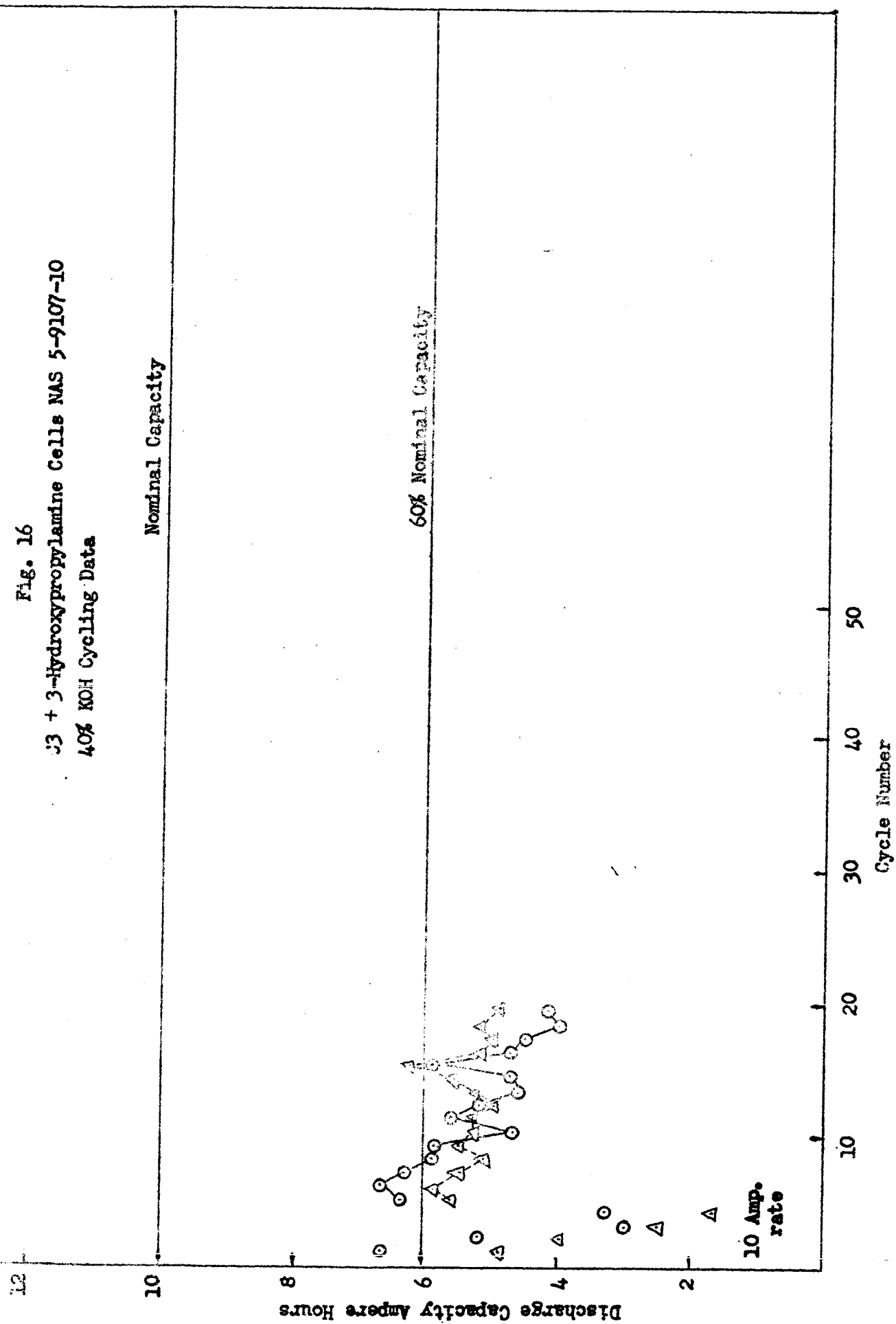




Fig. 17  
 B5 + 3-Hydroxypropylamine Cells NAS 5-9107-11  
 40% KOH Cycling Data

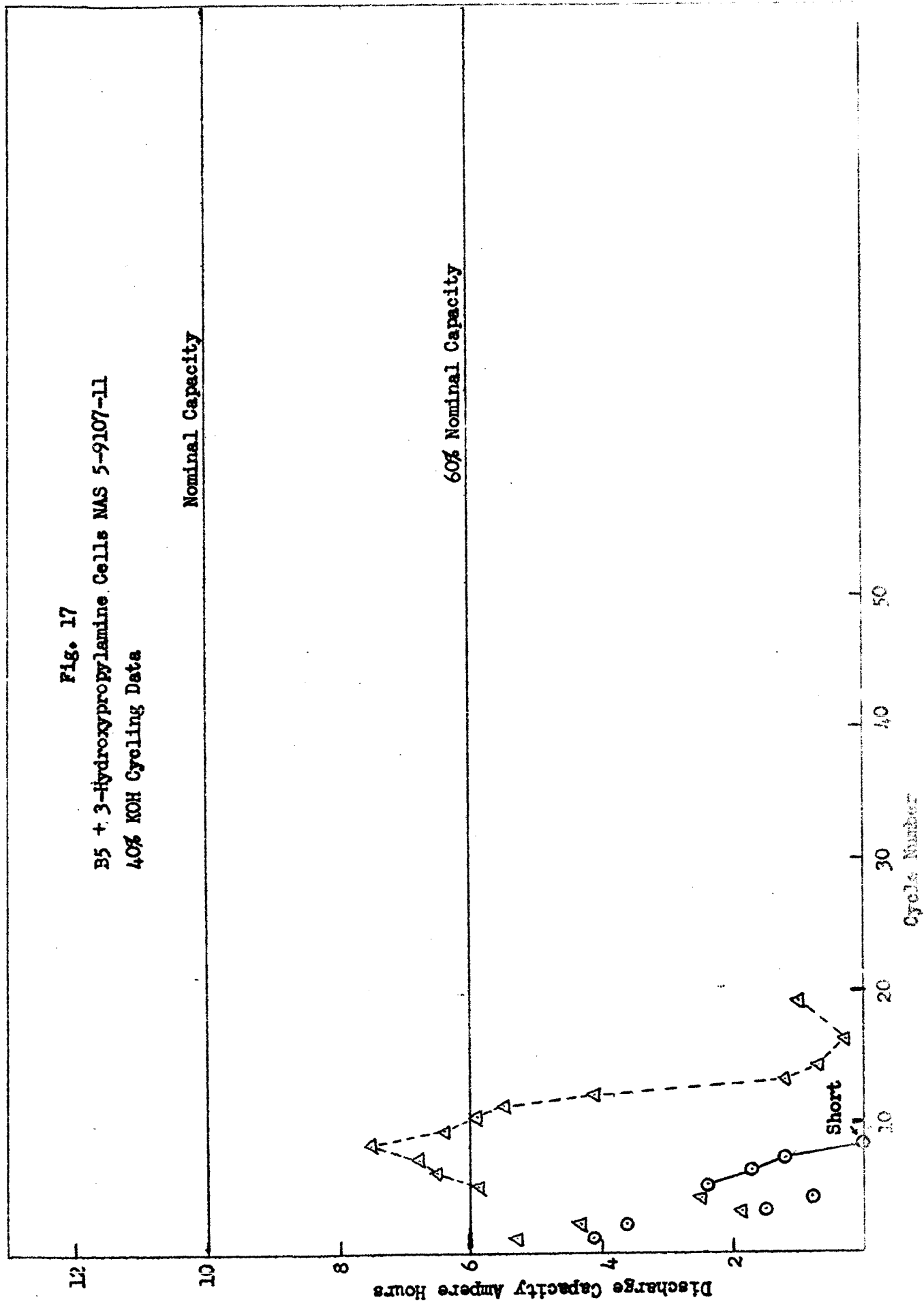


Fig. 18

C2 + 3-Hydroxypropylamine Cells NAS 5-9107-13  
40% KOH Cycling Data

Nominal Capacity

60% Nominal Capacity

10 Amp.  
rate

Test terminated

Cycle Number

Discharge Capacity  
Ampere Hours

12

10

8

6

4

2

10

20

30

40

50

